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RECENT DEVELOPMENTS IN FIRE PROTECTION DEVICES

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THE importance of fire protection engineering is perhaps best realized when we consider the annual fire waste of the country. In 1875 this was about $78,000,000; in 1885, $102,000,000; 1895, $142,000,000; 1905, $165,000,000; 1906 (the year of the San Francisco earthquake), $500,000,000. The figures for 1907 are estimated at $180,000,000, which is perhaps a fair average for the last few years.

America stands first in the list of countries in the amount of property annually destroyed by the fire fiend, and it is natural, therefore, we should stand first in the modern crusade against this destructive element. Figures showing the amount of money annually spent for this purpose would be extremely interesting, but they are difficult to obtain. They would include the cost of maintaining fire departments in all cities and towns; the cost of enforcing building laws, maintaining fire marshal departments, equipping and maintaining testing laboratories; the expense of insurance companies, with their numerous ramifications of inspection bureaus, rating organizations, etc.; part of the expense of ordinary water works systems; and lastly, the cost of equipping buildings with modern fire appliances.

First of all it should be realized that this fire waste constitutes an absolute destruction of property, $180,000,000 worth of property completely wiped out of existence every year.

It is often said that insurance companies pay the loss, if happily the loser is fully insured; but it is not always realized that insurance companies simply distribute the loss among many persons, but do not really pay it. They are nothing but banking institutions, receiving money from many and distributing it among a few. You and I, and every one who insures, are really the ones who pay the losses.

With this stupendous and constantly growing ash heap threatening our progress, it behooves every citizen to make himself familiar with the conditions and do his part toward improvement. No one would claim that the conditions cannot be improved, but few are sufficiently versed to know just what should be done. It is here that science is appealed to, as in so many of the practical problems, for a solution of the difficulty.

Modern fire fighting appliances, as used by fire departments, have already reached a high state of usefulness, but they are certainly not keeping pace with modern building construction. The recent fire in the Parker Building, in New York, is an excellent illustration of this fact. Here was a building of modern fire-resisting construction, twelve stories in height, located in the heart of the city. It was built for an office building but used as a printing establishment, and contained a large amount of combustible material. While this, no doubt, had something to do with the heavy loss, still the fact remains that after the fire had gained headway the firemen were powerless to cope with it, and it practically burnt itself out. Hose streams were utterly useless above the eighth story, and still this was in the heart of the largest city in the country, where the fire department is supposed to be second to none. With this condition of affairs in a twelve-story building, what are we to expect in the twenty, thirty, and forty-two story buildings of our large cities? It is only a matter of getting enough combustible material into these buildings at a high elevation, and enough of these buildings close together, and the conditions are ripe for an aërial conflagration where the modern fire department would be as helpless as in attempting to quench an eruption of Vesuvius.

Under such conditions the fire protection engineer is sought for advice. He is the product of the last quarter century, but his work is no less important than that of the older branches of engineering. Nearly all of the technical schools are turning out men to enter this profession, and their numbers are constantly increasing. In the city of Boston alone there are probably over one hundred such engineers. A fire protection engineer is usually found in the employ of the insurance interests, for

insurance companies have long since found it necessary to devote their attention to the lessening of fires. While they can adjust rates to cover any conditions, it is clearly for their interests in the long run, as well as that of the community at large, that the fire losses should be kept as small as possible. Their work may be briefly summed up as follows:

First, the investigation of methods of preventing fires; second, devising and supervising means of extinguishing them with as little loss as possible. The method of preventing fires we will not deal with at length. Suffice it to say that it is done by constant inspection of existing conditions, study of fires as they occur, and an effort to eliminate such conditions as favor the starting of fires.

Coming to the second point, the duties of the insurance engineer are principally along the lines of private fire protection, for it is believed that by getting improvements in individual plants, thus lessening the chance of a fire of large proportions, more can be accomplished than by endeavoring to produce appliances that will extinguish conflagrations. A fire in its incipiency is always easily extinguished, and by the aid of appliances that will give prompt alarm or bring the extinguishing agent into quickest use the greatest hope lies. It is perfectly possible to prevent such conflagrations as that in Baltimore, with its $50,000,000 loss, and the one in San Francisco, with its loss of $350,000,000, if the public would coöperate with the fire protection engineer. The remedy may be expensive, but it is certainly worth the money it costs.

These preliminary remarks may be enough to emphasize the importance of modern fire protection devices.

Historical Data

The first fire engine of which we have record was mentioned by Hero, 150 B.C. Such devices were, however, not used to any extent until about the seventeenth century. "Hand squirts" were first used in London about 1600, and flexible hose was introduced about 1672. Steam fire engines were invented in London about 1830, and first used in this country about 1853.

The first attempts at private fire appliances were along the lines of fire pails, and these, by the way, are even today considered of the greatest value. The larger manufacturing plants often installed steam pumps, which could be used to feed standpipes in the mills or hydrants outside. These were single cylinder pumps of the capacity of 200 to 500

gallons per minute, and gave very fair results if properly cared for and intelligently handled.

About the year 1870 perforated pipes began to be used. This form of protection consisted of a series of pipes running along the ceiling, located 8 to 12 feet apart and containing a series of small holes. These holes were so located that when the water was turned on a number of jets were thrown close to the ceiling, dropping to the floor below and wetting it more or less thoroughly. The piping on each floor was operated by a valve located outside the building, or in some other suitable location. In case of fire the proper valve was opened, provided some one was fortunate enough to be on the spot at the right time. This crude device gave very poor distribution as compared with modern sprinkler systems, and also had the defect of wetting down a much larger area than that covered by the fire. The holes also became readily clogged by dirt and corrosion.

AUTOMATIC SPRINKLERS

Automatic devices for the extinguishing of fires were not installed in a commercial way until about 1878, although experimental devices were made as early as 1864 and patents were issued much earlier. In 1806 John Cary patented a device consisting of "Rose" sprinklers, supplied by an elevated tank of water and controlled by a weighted valve which was operated by the burning of cords.

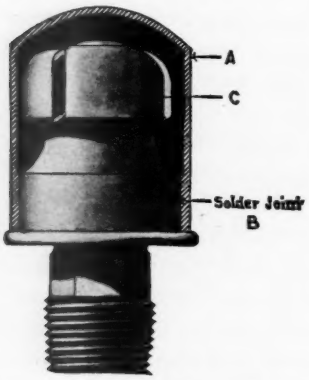

FIG. 1. — PARMELEE SPRINKLER
(Cap in Section)

"Water joint" type. The cap *A* is soldered at the point *B* and is full of water. The turbine *C* distributes the water when the head fuses and opens.

The first sprinkler head to be used commercially was the "Parmelee" (Fig. 1). This consisted of a revolving cylinder or turbine, containing slits through which the water could issue, the whole being covered by a cap which was soldered in place. The sprinklers were located about every 10 feet apart throughout the building, or the hazardous sections of the building, at a distance of 4 or 5 inches below the ceiling. They were connected to a system of piping which was kept full of water, fed by an

elevated tank, public water supply, or some other reliable source. Heat from a fire would fuse the solder, allowing the sprinklers to open and extinguish the fire. The solder melted about 160° F., which is the same melting point as is used today; but the head lacked sensitiveness for the reason that the solder joint was not insulated in any way from the long line of piping and the water was in direct contact with the joint.

It might be stated here that 155 to 160° is as low a melting point as is practical for solder. The formula is approximately as follows: bismuth, 4 parts; lead, 2 parts; cadmium, 1 part; tin, 1 part. This formula is based on patents granted Barnabas Wood in 1860.

Sir Isaac Newton in 1799 discovered that certain alloys melted lower than their constituents. The melting points of some of the component parts are as follows: bismuth, 476°; lead, 504°; tin, 421°.

Any solder melting at a lower temperature contains mercury, which deteriorates with age. Furthermore, this temperature is considered low enough; solder fusing much lower than this is liable to give way in very hot weather. When repeatedly heated nearly to its melting point, solder is subject to cold flowage, especially if under strain. For this reason it is considered wise to allow a leeway of about 50° F. between the highest temperature to which the room is subjected and the melting point of the solder used at that location. In dry rooms and other places where high temperatures are found a higher fusing solder is used; the common types found on the market melt respectively at 212, 286, and 360° F.

The rules for the installation of automatic sprinklers cover forty-three pages and are becoming more complicated all the time. Still, in the important features they have changed but little since the early installations. The rules for spacing state that heads shall be located not over 10 feet apart under smooth ceiling and not over 12 feet apart in 8-foot bays or less. In other words, one head is supposed to cover an area not exceeding 100 square feet. In the matter of pipe sizes, there have been more changes. In the early equipments, one head was allowed to be fed by a ¾-inch pipe; three heads by a 1-inch pipe; six heads by a 1¼-inch pipe; ten heads by a 1½-inch pipe, etc. Under the present rules, one head is allowed on a ¾-inch pipe; two heads on a 1-inch pipe; three heads on 1¼-inch pipe; five heads on 1½-inch pipe, etc.

Piping is supported from the ceiling at an elevation such that the deflectors of the sprinklers shall be between 3 and 10 inches below the bottom of the joists or surface of the ceiling. The heads are arranged to cover every nook and corner, so that a fire cannot start at any point

without having a sprinkler head within 5 feet of that point (measured horizontally) ready to open when heated to the proper temperature.

Amongst the early sprinklers may be mentioned the Brown, Burritt, and Bishop, all being of a type somewhat similar to the Parmelee.

The next step in advance was the removal of the solder joint from contact with the water, thus making the head more sensitive. The Brown,

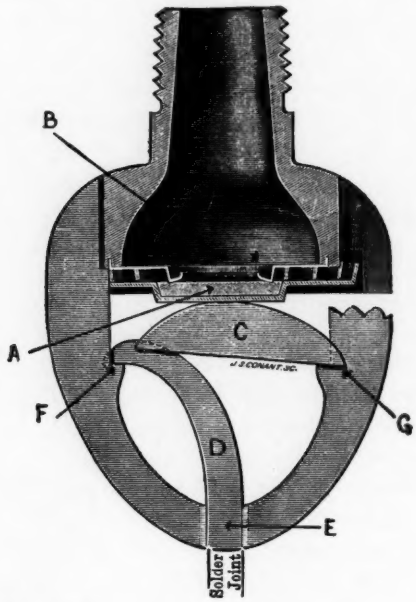

FIG. 2.—GRINNELL "METAL SEAT" SPRINKLER
(Sectional View)

The valve *A* is held against the outlet *B* by the levers *C* and *D*. The solder joint is at *E*. The valve seat and deflector are all one piece, and when the head fuses this falls as far as the notches *F* and *G*, on which the levers rest.

Burritt, and Bishop heads were all developed along these lines, but the Parmelee was superseded by the Grinnell (Fig. 2). This latter is perhaps the most interesting of all sprinklers, for it is the one having the largest sale here and abroad, and is installed by the largest sprinkler company. In fact, the inventor, the late Frederick Grinnell, was the most important factor in the sprinkler business in America. Starting in the steam fitting business, he became interested in sprinklers, and at first installed the Parmelee head. About 1882 he first put out the Grinnell head. This

was probably the first sprinkler to use a splash plate or deflector for distributing the water, and it contained many other novel features, including a flexible diaphragm, lead disks, etc. This sprinkler later developed trouble by sticking at the valve, and three other types followed between 1884 and 1890. In the second, a block-tin disk was used. In the third, the same disk was used, but the seat ring was narrowed. In the fourth, a babbitt disk was used.

Other sprinklers used about this time were the Kane, of which there

FIG. 3. — GRINNELL "GLASS DISK" SPRINKLER
(Sectional View)

The glass disk, or button, closes the outlet which is in a thin metal sheet. The glass disk is held in place by the vertical strut composed of three pieces of metal soldered together. This strut falls away when melted, allowing glass disk to be pushed out by the water, which then strikes the toothed deflector and is properly distributed.

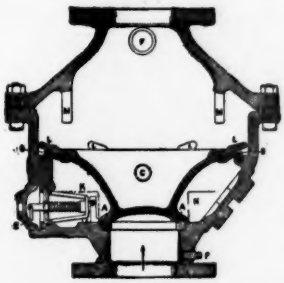

FIG. 4. — OLD GRINNELL DRY VALVE
(Sectional View)

The movable valve *LLAA* has an air seat at *BB* and a water seat at *AA*. The intermediate space *K* is not under pressure. The air seat is about eight times the area of the water seat, so that one pound of air will hold back about eight pounds of water. The latch *E* holds the valve open after it has tripped and prevents water columning.

are many types; the Neracher, which is now controlled by the General Fire Extinguisher Company; the Ruthenburg; and the Walworth.

In the original Walworth head, the movable arm was soldered to the frame, but later the arm was held by a fusible link, which made it much more sensitive.

About the year 1890, further improvements were made in sprinkler construction, and it is from this time that the general type used today may be said to date. The Grinnell glass disk head (Fig. 3) appeared in 1890; International the same year; Manufacturers', 1893; Hibbard, 1894.

In the Grinnell glass disk head the seat is of glass, thus effectually preventing corrosion at this point. The valve is held closed by a strut built up of three sections soldered together, a great improvement over the old lever type of support. The head was smaller and greatly improved in appearance over the earlier types.

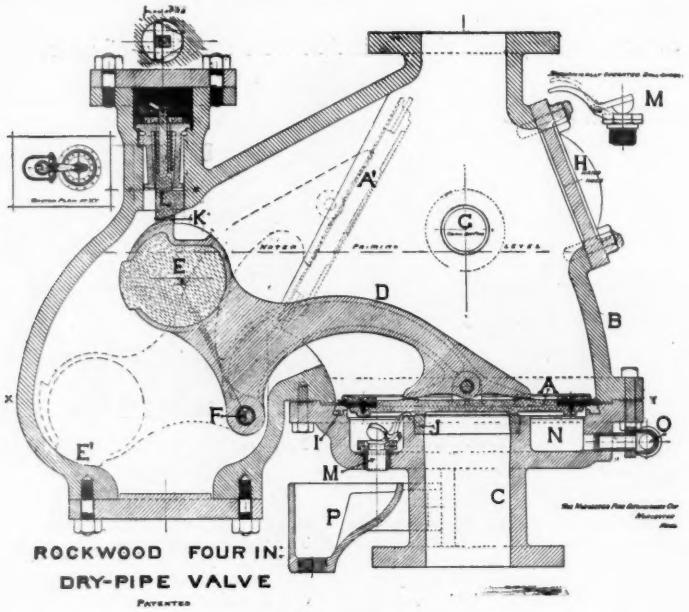

FIG. 5. — ROCKWOOD DRY VALVE
(Sectional View)

The valve *A* is attached to an arm *D* pivoted at *F*. It has an air seat near *I* and a water seat near *J*, the former being about eight times the area of the latter. *H* is a removable hand plate and *L* is a latch to prevent the valve from seating after it has opened.

Since 1890 there have been numerous improvements in details, but the general principles involved remain practically unchanged.

There have been some 363 patents issued on sprinklers in the United States, and a large number have been built that were never patented. Of all this vast array, only seven remain on the list approved by the National Board of Fire Underwriters today.

The modern sprinkler head is a well-developed device and very reliable in its action. Further developments may come, but it does not seem likely

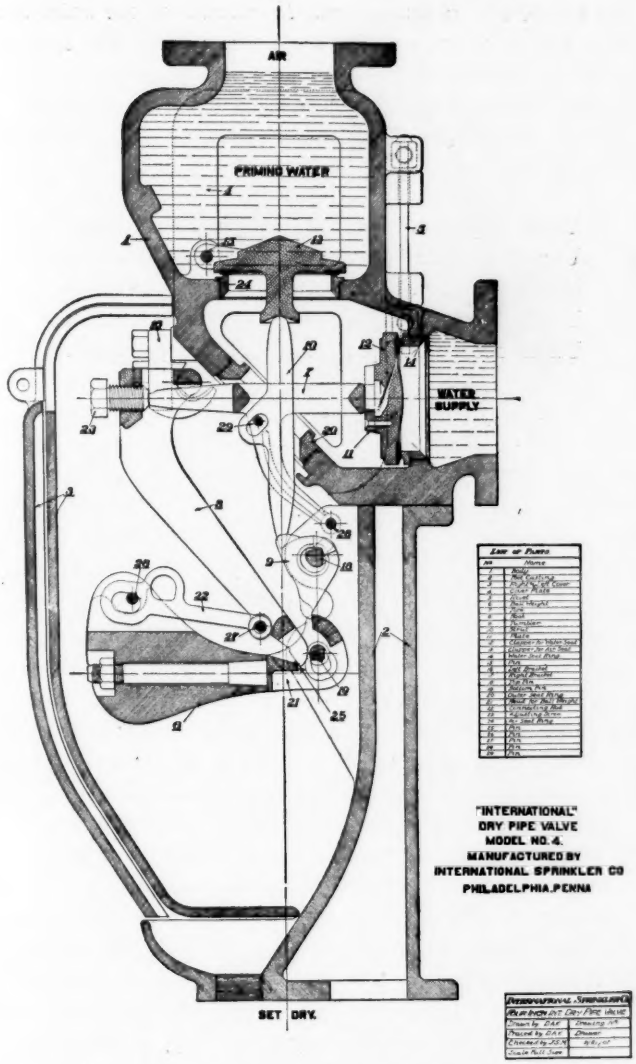

FIG. 6. — INTERNATIONAL DRY VALVE
(Sectional View)

The water valve 11 is held in place by a series of struts and levers 7, 8, 6, 9, and 10 bearing finally on the air valve 13. This leverage gives a differential of about 6 to 1 between the air and water seats. A little priming water is shown above the air valve in order to give a tighter joint.

that they will be of a radical nature. It will not corrode under ordinary conditions, that is, where no acids are present; and it will open as it is designed to do when heated to the proper temperature.

The amount of water delivered under different pressures may be of interest. The modern sprinkler has an outlet of ½-inch diameter and will discharge approximately the following:

Under	5 pounds	pressure	12 gallons per minute
Under	15 pounds	pressure	21 gallons per minute
Under	30 pounds	pressure	30 gallons per minute
Under	75 pounds	pressure	50 gallons per minute
Under	100 pounds	pressure	58 gallons per minute

Dry Valves

Sprinklers are often installed in buildings where there is no heat and where the water in the pipes would freeze. In the early stages of sprinkler protection, the dry valve was invented for this contingency, and it is now a very important factor. There are several approved designs, but the main idea in each is to supply a mechanism for holding back the water by means of compressed air under a lighter pressure than the water. Of course it is perfectly possible to install an ordinary swing check valve and pump a heavier air pressure above it than there is water pressure below. The trouble with this scheme is that it is difficult to maintain piping tight under an air pressure of 100 or 150 pounds, and furthermore it takes too long to let this air pressure out of the pipes after a sprinkler head has opened. The rush of air fans the fire, and the time when the water can reach the outlet is greatly delayed.

The simplest form of dry valve, the old Grinnell (Fig. 4), is a differential check valve. The upper or air seat is about eight times the area of the lower or water seat, and between the two is an intermediate space which is not under pressure. This intermediate space is used to actuate the alarm-giving device when the valve opens. A later development of this idea is found in the Rockwood dry valve (Fig. 5), where the valve is compressed into a single disk with two seats, and the whole placed on an arm which swings entirely out of the water way when open.

In the International valve (Fig. 6) we have the water seat held closed by a system of levers, and in the Manufacturers' valve (Fig. 7) a somewhat similar arrangement.

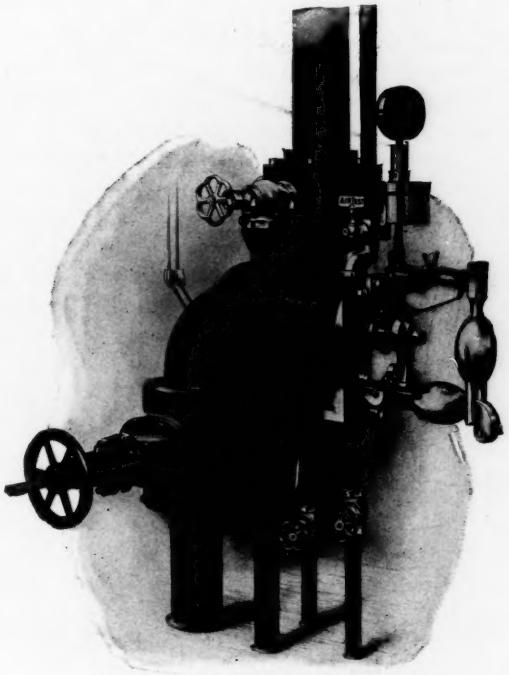

FIG. 7. — MANUFACTURERS' DRY VALVE
(Exterior View)

This valve has a separate water and air seat. The water seat is held in place by a system of levers and weights which bear finally on a piston in the chamber below the gage. This piston is held down by air pressure piped from the system on the floor above.

ALARM VALVES

Early in the art of sprinkler protection it was found that some form of alarm device was very desirable in a sprinkler system. Such a device will prevent a sprinkler system from doing a heavy water damage, as, for instance, in case a sprinkler should be opened by fire, and the fire extinguished by it when no one was in the building. There have been many cases where this has happened or where a sprinkler operated from some other cause, and where the trouble was not discovered until the system had been running for many hours. Where there was a dry valve, it was easy to arrange an alarm connected to this. For instance, the filling of the intermediate space in a Grinnell dry valve could be utilized

to make an electrical contact as well as to ring a rotary gong run by water power. Where there is a wet pipe system a separate alarm valve is required for this purpose. The early types consisted of ordinary check valves with a packed stem extending through the casing and connected by an arm to some form of electric contact-closing device.

The trouble with these was twofold. First, the possible sticking at the packed stem; and second, the danger of false alarms due to water hammer. These defects have been practically solved in the modern approved valves, the Grinnell and the International (Figs. 8 and 9).

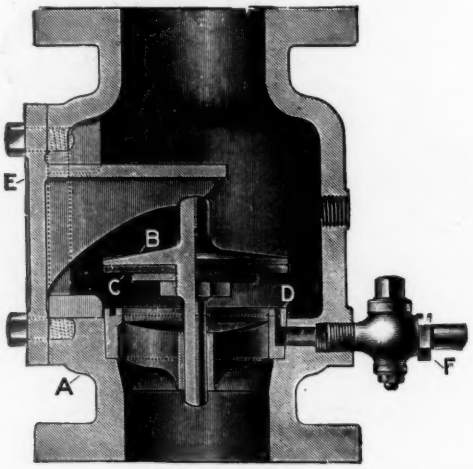

FIG. 8.—GRINNELL "VARIABLE PRESSURE" ALARM VALVE
(Sectional View)

The vertical check valve *B* bears when closed on a grooved seat *D* and closes the groove. When it opens, the water passes into the groove and hence through pipe *F* and interrupting pot to electric circuit closer or water motor gong (not shown).

WATER SUPPLY

Let us now consider the water supplies for these systems. The insurance rules always require two separate sources of water supply for minimum rate, for it often happens that one supply will become crippled. Thus, street mains may break, tanks may be drained by leaks, and pumps may break down. A reliable system of water works is usually the most satisfactory source of supply, provided the pressure is sufficient. This pressure should be such as to give at least fifteen pounds at the highest point in the system.

Gravity Tanks are used very commonly as a source of supply. Formerly, a 5,000 gallon tank at an elevation of 12 feet above the roof

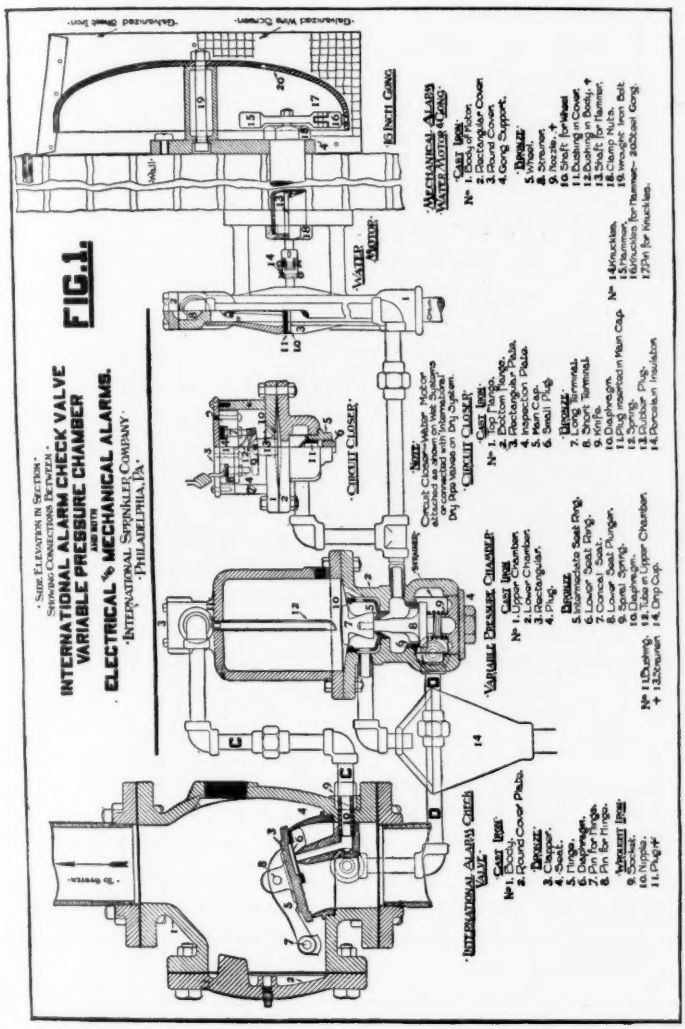

FIG. 9. — INTERNATIONAL ALARM VALVE
(Sectional View)

The swing check valve 3 tightly closes the outlet of pipe *C* when on its seat. When the check opens, water flows through pipe *C* to variable pressure chamber, hence to electric circuit closer and water motor.

was considered a satisfactory supply for moderate sized buildings, but today the usual size is 10,000 to 15,000 gallons, with an elevation of 15

to 20 feet. Flat iron hoops were formerly used, but round painted hoops are the standard today. In large plants, tanks as large as 200,000 gallons are installed at elevation up to 200 feet. These large tanks are of steel, on trestles of the same material. In Charlestown there is a tank of 100,000 gallons, on a 200-foot trestle, feeding sprinklers in the Boston & Maine grain elevator. The top of the tank is higher above ground level than is Bunker Hill Monument above the level of the hill. Concrete tanks are also being installed to some extent, and they have the advantage of cheap maintenance. A firm in Boston is now building two concrete tanks, one being 50,000 gallons' capacity on a 100-foot trestle, and the other 100,000 gallons on a 150-foot trestle.

Pressure Tanks are occasionally used, especially where the other source of supply is under light pressure. These are built of boiler iron, with joints tightly caulked to withstand a heavy pressure. They are filled two-thirds full of water and then sufficient air is pumped in so that when the last water is being discharged from the tank it will give a pressure of fifteen pounds at the top of the building. This means a pressure of seventy-five pounds if the tank is at the roof level, and a higher pressure if it is at a lower level.

These tanks have been used for about twenty-five years, and there has been but little development except in size. The early ones had a capacity of 2,000 to 4,500 gallons, while today tanks of 7,500 and 9,000 gallons are being installed. The Macy Department Store in New York has a complete sprinkler system of over 11,000 heads, supplied by six 10,000-gallon gravity tanks and six 6,000-gallon pressure tanks.

Steam Pumps.—Pumps are also a common source of supply, and there has been a striking development in these devices in the last twenty-five years. The old steam pumps were single cylinder affairs, poorly designed to deliver a large volume of water at short notice after lying idle for many months. The modern Underwriter steam pump is designed especially for fire service, with bronze pistons and plungers, stuffing boxes, brass-lined, large area valves, large steam and exhaust passages, large suction, wrought iron side levers, etc. As a part of the pump are required capacity plate, gauges, vacuum chamber, relief valve, priming pipe, hose valves, etc.

Automatic regulators are frequently required with steam pumps, and these, too, have undergone a radical development. The type most used was practically designed by an insurance engineer, and is particularly fitted for fire pump work.

Rotary Pumps.—Rotary pumps are frequently used for fire protection, especially where there is plenty of water power and little or no steam available. In the older types there was an undue opportunity for corrosion, large friction loss, considerable variation in pressure, and other undesirable features. In the National Standard Rotary pump, the specifications for which were only recently drawn up by a committee of the National Fire Protection Association, these defects have been

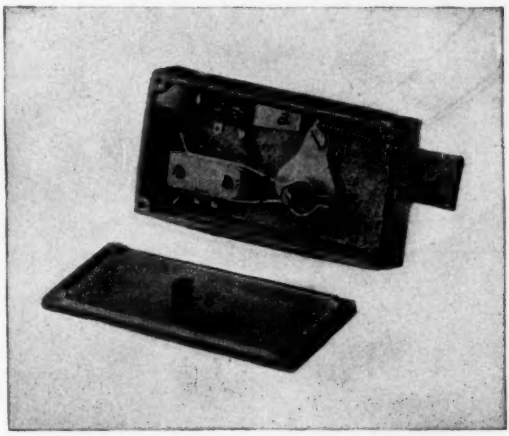

FIG. 10.—A. D. T. CO. GATE VALVE ATTACHMENT

c = case; *d* = case contact; *e* = rubber roller; *ff* = German silver springs; *g* = post for closing case contact.

This is designed to attach to a gate valve so as to give an alarm as soon as any one starts to close the valve.

largely eliminated and numerous attachments, such as air chamber gauges, hose connections, etc., are included in the requirements.

Other Pumps.—Electrically driven pumps, both of the plunger and rotary types, are occasionally used, and specifications have been made covering all details of these. Within a very few years centrifugal or turbine pumps have been built for fire purposes, but the insurance interests have not yet promulgated any specifications for their construction. They are, however, extremely well adapted for electric driving where the suction is under a head, and they will, undoubtedly, be a considerable factor in the future.

Sprinkler Supervision

Automatic sprinkler protection has become so highly developed that very few fires in buildings so equipped are not properly controlled. There are occasionally failures, but these are almost always due to one of the following causes:

1. Gate valve on system closed.

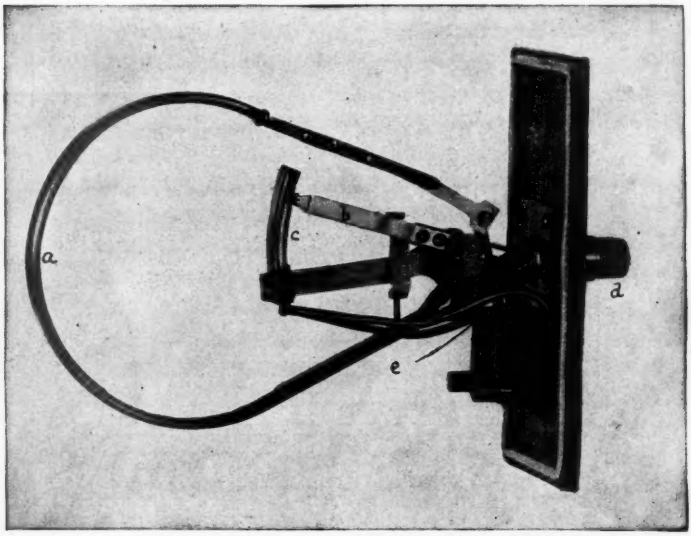

Fig. 11. — A. D. T. System, Pressure Device

a = Bourdon spring; b = lever operating Bourdon spring; c = contact springs; d = pipe connection to pressure tank or dry system. This is designed to be attached to a pressure tank or dry sprinkler system and to give an alarm if pressure falls below a predetermined point.

2. Water supply out of commission, due to empty tanks, crippled pumps, or freeze up.

To reduce these sources of failure to a minimum, sprinkler supervisory systems have recently been placed on the market.

The object is to connect all gate valves, alarm valves, tanks, etc., with electric circuits running to a central station, and so arranged that as soon as a valve is closed, the water in a tank becomes too low, or the temperature in a tank nears freezing point, etc., an alarm is transmitted.

To accomplish this, a closed circuit system is used, all wiring in the

building being in conduit, so that it cannot be tampered with. This conduit runs direct to a circuit breaker fastened to each valve and adjusted so that when the valve is turned more than a specified amount the circuit is broken and an alarm is transmitted.

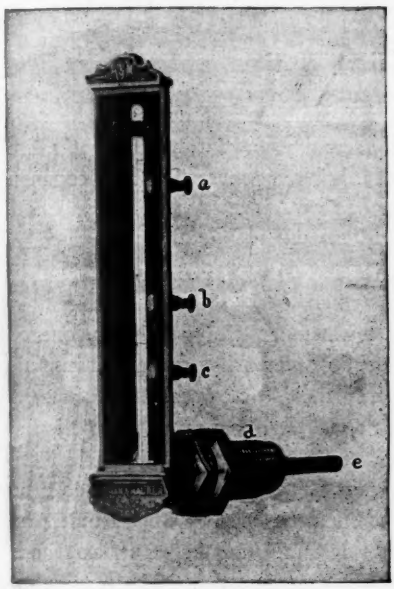

FIG. 12. — A. D. T. TEMPERATURE DEVICE

a = high temperature contact binding post; *b* = low temperature binding post; *c* = constant binding post.

This is designed to attach to a gravity tank to give an alarm in case pressure nears boiling point or freezing point.

In a similar way floats and thermometers are attached to gravity tanks, pressure gauges to pressure tanks, etc., and the whole is arranged so as to be practically tamper proof.

Men are kept on duty at the central station, and in case an alarm is received, a runner is dispatched to investigate the trouble and remain until conditions are restored to normal, if circumstances require it.

With such a system properly installed and maintained, the chance for failures in sprinkler systems will be small.

STATISTICS

Before leaving the subject of automatic sprinklers it might be interesting to consider some statistics.

In the city of Boston there are 175 buildings equipped with sprinklers. In 1906 there were thirty fires in these buildings, entailing a loss of $5,723, or less than $200 per fire.

In New England there are probably between 3,000 and 4,000 plants equipped, some being large mills covering many buildings.

The National Fire Protection Association statistics for ten years, covering over 5,000 fires in buildings equipped with sprinklers, show that 74.5 per cent. of the fires operated eight sprinklers or less, and that 93 per cent. of the fires were extinguished or properly held in check by sprinklers.

The General Fire Extinguisher Company, of Providence, has installed over 10,000,000 sprinkler heads, and it is estimated that perhaps 25,000,000 have been installed by all sprinkler companies in this country. This represents an investment of nearly $75,000,000.

ALARM SERVICE

Fire protection is never considered complete without some form of alarm service. This service, in a general way, aims to prevent a fire from gaining great headway before being discovered. The common forms of alarm service are:

1. Watchman service.
2. Automatic alarm or thermostat systems.
3. Alarm valves on sprinkler systems.

Watchmen's Service.—There are watchmen and watchmen, one of the commonest type being the old employee who has passed his usefulness, as well as his youth, and is given the job of watchman because it is easy, and he is not good for much else. Another common type is the foreigner, whose chief recommendation is the low price at which he can be hired. There are, of course, many efficient watchmen who do their work well, but in no case can a watchman be depended upon unless he makes a record of his rounds. These rounds should be at least once an hour, as called for by the Insurance Requirements. The temptation to take a nap when the rest of the world is sleeping is too great for the average man when no checking system is employed.

The first forms of watchman's clocks were portable affairs containing dials which revolved with the hour hand. Keys were located at different points, and at each station the key was inserted in the clock and turned, thus embossing or puncturing the dial. Each morning the dial was removed and a new one inserted.

These keys were easily duplicated, and many a watchman has remained comfortably seated in the warm engine room, making his records without moving from his chair. In some cases the keys were removed from their stations and carried to the watchman's headquarters for safe keeping during the night. Others have gone so far as to unlock the clock and make an entire night's record at once, thus leaving the whole night free for an uninterrupted nap.

The next development was the electric clock, which was located permanently in the office or other suitable place. Wires were run from

here to each station and connected with a battery, so that when the button was pressed at the station an electric circuit was made and a dial punctured on the clock. This led to some of the brighter watchmen studying electricity and finding out how, by short circuiting the wires, the same result could be obtained without traveling to the distant stations.

Then came the Magneto systems, where a small magneto was located at each station and the handle at that point had to be turned in order to generate the current to puncture the dial. This effectually prevented "beating" the clock by the watchman, but still left an opportunity for improvement; for if a watchman was taken sick early in the evening, or perhaps dropped dead, nothing was known about it by his employers until the next morning. Meanwhile his duties as a watchman were not being performed. This led to the central station watchman's service, which has been used for several years. With this system there is no local clock, but the wires are run to a central station, such as that used for sprinkler supervision, and recorded on a tape machine similar to that used to record telegraphic messages. There is some one on duty at all times, and if the signals do not come in on time (a certain leeway always being allowed) a man is sent from the central station to investigate. This system is usually combined with a fire alarm system, so that by breaking the glass and pulling a hook a fire alarm can be sent in from each watchman's station.

Thermostat Alarm.—Automatic thermostats have been in use since about 1870. Various principles have been employed for this purpose. An ordinary thermometer with a platinum wire fused into the glass at where the mercury column would make contact with it when the temperature became excessive was one of the first, and this principle is still used. The device is, however, expensive and bulky, and has never been popular.

The first Watkins thermostat contained two small strips of dissimilar metals, such as brass and iron soldered together. When heated, these metals expanded unequally, thus causing the strip to bend. When sufficiently heated, the strip came in contact with a platinum point and made an electric circuit. This same principle has been used in all the various types of Watkins thermostats, from 1873 down to the present time.

The first type of thermostat made by the American Fire Alarm Company was patented in 1884, and consisted of a U-tube containing mercury, with the short end open. When heated, the mercury overflowed the tube and made electrical contact in a cup below. This was

bulky, fragile, difficult to adjust accurately, and liable to failure, owing to oxidation of the mercury. In 1885 it was superseded by the ether tube thermostat, which was used in various forms up to 1900. In this a curved bourdon spring is used, which is filled with ether and tightly sealed. When heated, the ether expands and causes the tube to straighten out and thus make electric contact.

Other old types contained coiled springs, expansive wax, etc.

About 1898 the solder release principle came into prominence, although it had been used much earlier in the "United States" and in other devices.

The objection to the earlier solder release types was that they were not sensitive enough, and when installed in the same plant with sprinklers the latter might operate first and cool the air so that no thermostatic alarm would be given.

Later types were made more sensitive by making the soldered joint small and insulating it from the rest of the device. As before stated, the lowest melting point for a permanent solder is about 160°, so that the same kind of solder had to be used as for sprinklers.

The only approved devices in New England today are the Wall and Woodman, both solder release devices, and the Watkins, where two dissimilar metals expand unequally.

Thermostats are installed in a somewhat similar manner as sprinklers, being attached to the ceiling and located 10 feet or less apart. The wiring is on a duplex system, so that the current can come two ways and one break will not cripple the system.

The Underwriters require a daily test of the system with records, but this testing device, together with the transmitting devices, is rather too complicated to explain at length here.

In cities the alarm is usually given at a central station, but in smaller towns and in the country it may be received at fire department houses, or at bells located in dwellings. An annunciator showing from which floor the alarm is received is attached to the outside of the building, except in central station equipments where the floor number is transmitted after the alarm. With central station system, a closed circuit is generally used.

FIRE DOORS, SHUTTERS, ETC.

Another important department of fire protection engineering covers the protection of buildings against a fire from outside. Up to the present, nothing has been discovered in the way of an economical building material

which is superior to brick as a fire retardent. A parapet brick wall, without openings, is, therefore, ideal for this purpose. Unfortunately, windows are often necessary, and the problem then becomes one of finding a suitable material for covering these windows.

Iron shutters about ¼ inch thick were the first to be used extensively. It was found that these warped in a bad fire, and they were finally replaced, to a large extent, by wood shutters, tin covered. These have been improved in regard to the joining of the tin, the kind of hardware used, etc., but the same general principle is used today.

This principle is, that if wood is covered so that the air cannot reach it, no combustion will take place. The reason for using wood is that it is cheap, easily worked, and of the required stiffness. The shutter is made of two thicknesses of ⅞ inch boards laid at right angles, then covered with double lock-jointed tin put on so that each joint is locked and no nail holes are exposed. When heated, the wood gradually carbonizes, but so long as the tin remains in place, it cannot burn. Such a shutter will stand a temperature of 1,500 to 1,700° F. for an hour and still hold its shape.

Fire doors are built on the same principle, except that three thicknesses of wood are now required. These are of larger area than shutters, and two thicknesses were found insufficient to withstand a severe fire.

Numerous other doors and shutters have been put on the market of late years, built of asbestos board, paneled steel, cement-filled metal, etc., but none that are of standard fire-resisting qualities are cheap enough to come into general use.

Wired Glass

Wired glass windows in hollow metal frames have been used for the past six or eight years, and are replacing shutters to some extent. They have the advantage of being more easily closed, and, furthermore, they are more apt to be closed when needed. They are as good a fire retardent as shutters, except for the fact that they transmit heat readily.

Combustible material located within a foot of the glass can readily be set on fire by radiated heat, but if there is no combustible material near by, these windows form a very satisfactory fire stop.

Wired glass is ¼ to ⅜ inch thick and contains a coarse wire netting embedded in the centre. It can be heated almost to red heat and have water thrown upon it without breaking apart. The glass is cracked into thousands of pieces, but the wire netting holds it in place.

There are detailed rules for the construction of the sash which we have not time to consider.

Open Sprinklers

Another form of protection for windows is open sprinklers (Fig. 13). These are specially designed sprinkler heads, with outlet open at all times, arranged to be placed at the top of a window or under a cornice. They are also made for the peaks of shingle roofs. The piping is arranged in a somewhat similar manner as with automatic sprinklers, but the main valve is kept closed and only opened in case of fire. While they are of considerable value, still the protection they afford cannot be considered the equivalent of standard shutters or wired glass windows.

Fig. 13.—Grinnell Open Sprinkler

Designed to be placed at top of window or under cornice and form a water curtain on the exterior of a building.

HOSE, HYDRANTS, ETC.

Considerable might be said in regard to hose, hydrants, play pipes, and fire department apparatus, but time does not permit.

Leather hose was used up to thirty or forty years ago, when linen and rubber replaced it. The standard today is cotton, rubber-lined, and the specifications call for high grade rubber of a considerable thickness. The modern play pipe for use in private plants is of brass, 30 inches long, with tapered outlet 1⅛ inches in diameter. The whole is wound with painted cord and fitted with swivel handles. The monitor nozzle is used considerably on the roofs of high buildings, in large, high-studded sheds where sprinklers are not entirely feasible, and in other places.

The modern steam fire engines are familiar to every one, and their size and capacity are constantly increasing.

Chemical extinguishers are also used extensively by fire departments, and the smaller types give excellent protection in factories and dwelling houses. They, too, have been greatly improved since they were first used, thirty or forty years ago.

In closing, I would like to make a few practical suggestions for lessening the annual fire waste and the fearful loss of life which it entails. Such horrors as the Iroquois Theatre fire, the steamship *Slocum* disaster, and the recent school fire in Collinwood can be prevented, and it is largely a matter of arousing public sentiment in order to have the necessary remedies applied.

First, prevention of fires. This is a matter that lies almost entirely in the hands of individuals. No fire department, no sprinkler system, no device of any kind can prevent a fire from starting. Fires are caused largely by carelessness. If every one should see that no rubbish is allowed to accumulate on his premises, that all oily waste is burned before it ignites spontaneously, that stoves and furnaces are properly arranged, that only safety matches are used, and that all other cautions that common sense dictates are strictly adhered to, we should at least have made a good start.

Second, the prevention of the spread of fire. This can be done by improved construction, by improved private protection, and by maintaining the most efficient fire departments. If every owner of a fire trap should equip it with automatic sprinklers, and if every owner of a well-constructed but exposed building should protect all window and other outside openings in a standard manner, then conflagrations would be practically eliminated. It is perhaps too much to hope that such improvements can be made by the free will of the owners, but it is perfectly practical to pass laws which will require it. Theatres can be made safe by equipping the stage section with automatic sprinklers, installing approved automatic vents over the stage, and making a proper fire cut-off between the stage and auditorium by means of fire doors, asbestos curtain, and water curtain. Schoolhouses can be made safe by building them first of fireproof construction, or by placing automatic sprinklers in all sections where a fire is liable to start, and then putting stairways in cut-off towers, etc. It is only a matter of arousing public sentiment, and these improvements will be forced upon those who are responsible for these conditions.

The cost of these changes is not prohibitive; in fact, in most cases it is entirely offset by the reduction in insurance rate.

Refuse to patronize unsafe theatres, refuse to send your children to schools that are fire traps, refuse to travel in crowded excursion boats which are entirely without adequate fire protection, and you will be doing your part toward preventing the recurrence of these disasters.

CONTRIBUTIONS FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
No. 31

AN IMPROVED APPARATUS FOR THE MEASUREMENT OF TRANSFERENCE NUMBERS IN SOLUTIONS OF THE HALOGEN ACIDS AND THEIR SALTS

BY EDWARD W. WASHBURN

I. INTRODUCTION

THE apparatus and method described in this communication were devised for the purpose of studying the true transference numbers and relative ionic hydrations in solutions of the alkali chlorides, an investigation which required the application of the Hittorf method with the highest possible accuracy. Since the apparatus is of general applicability in transference experiments by this method, and as it embodies several improvements over previous forms, it has seemed desirable to describe it at this time, leaving for a future communication the results of its application to the study of the problem of hydration in solution.

The conditions which must be fulfilled in order to attain the highest degree of accuracy in a transference measurement by the Hittorf method may all be summed up in the following statements:

1. The passage of electricity from electrode to solution or from solution to electrode must take place by one path only, that is, side reactions and partial secondary reactions must be excluded.

2. The amount of electrolyte transferred and the concentration changes resulting at the electrodes should both be as large as possible.

3. The amount of electricity passed through the solution must be accurately known.

The first condition depends upon the nature of the electrodes, while the second condition, once the electrodes are determined, is dependent chiefly upon the form of the apparatus used. We shall proceed to the consideration of each condition separately.

II. The Electrodes

If a solution of an alkali chloride be electrolyzed between platinum electrodes, hydrogen and hydroxyl ions are formed at anode and cathode, respectively. These rapidly moving ions soon migrate away from the electrodes and mix with the electrolyte in the middle portion of the solution. To avoid the formation of hydrogen ion, Hittorf[1] used a cadmium anode, placing it at the bottom of his apparatus. The slowly moving cadmium ions which formed around this electrode effectually prevented any stirring. This use of a soluble anode (usually cadmium or zinc) to avoid the formation of hydrogen ion was followed also by Hopfgartner,[2] Bein,[3] and Jahn[4] in their investigations. According to Bein, the use of these soluble anodes is complicated by side reactions resulting in the formation of basic salts. This statement, however, is contradicted by Jahn, who could find no evidence of any such action.

To prevent the formation of alkali at the cathode, Hopfgartner and Jahn used a mercury electrode covered with a layer of a strong solution of the salt of some metal which amalgamated readily with mercury, usually zinc or copper. These devices effectually prevent the formation of the rapidly moving hydrogen and hydroxyl ions and the evolution of gas at the electrode. (This latter effect is to be avoided, owing to its tendency to produce stirring and to carry away mechanically a portion of the solution in the form of a fine spray.) They have the disadvantage, however, of introducing foreign ions into the solution, thus preventing a large transport of electrolyte and complicating the analyses. Noyes,[5] in his investigation of the transference numbers of the alkaline-earth metals, modified the method by making both electrodes of platinum and by adding during the electrolysis, at the anode and cathode, respectively, measured quantities of alkali and of acid, so as to keep the solution at a uniform concentration and to prevent the formation and migration away from the electrodes of hydrogen or hydroxyl ion. By this means he was able to obviate the above mentioned difficulties and to obtain a much larger transport of electrolyte than any of the previous investigators.

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[1] Hittorf, Pogg. Ann., **106** (1859).

[2] Hopfgartner, Z. physik. Chem., **25**, 115 (1898).

[3] Bein, Z. physik. Chem., **27**, 1 (1898).

[4] Jahn, Z. physik. Chem., **37**, 675 (1901).

[5] Noyes, J. Am. Chem. Soc., **23**, 148 (1901).

Obviously the ideal electrodes to use in a transference measurement would be composed of the metal whose salt was under investigation. The process then would consist simply in the formation of the metal ion at the anode and its discharge at the cathode, accompanied by the transference of T equivalents of the salt from one electrode to the other. While in the case of the alkali halides we cannot use the reversible metal electrodes, we can attain the same result by using reversible electrodes composed of the corresponding insoluble halide salt of some other metal, such as silver. Thus, if one equivalent of electricity be passed through a sodium chloride solution between silver chloride electrodes, or more strictly speaking between a silver anode and silver chloride cathode, the process which takes place consists essentially in the formation of chloride-ion at the cathode and its discharge at the anode where insoluble silver chloride is formed. At the same time T equivalents of electrolyte are transferred from anode to cathode, T being the transference number of the cation. By means of this simple arrangement it is possible to carry on the electrolysis without the formation of any acid or alkali, or the evolution of any gas, or the introduction of any foreign substance into the solution. The present investigation has dealt only with the preparation and use of silver chloride electrodes. A few qualitative experiments with silver iodide and bromide electrodes, however, indicate that when prepared in an analogous manner they also will give good results.

Preparation of the Silver Anode.—The use of a silver anode[1] for transference work with solutions of chlorides was introduced by Noyes and Sammet[2] in their transference measurements on hydrochloric acid. If a solution of a chloride be electrolyzed, using a silver rod as the anode, the following series of phenomena take place. The bottom of the rod is first attacked and a coating of dark gray silver chloride is formed, which extends slowly upward until the rod is entirely covered. The layer gradually increases in thickness, and the potential between electrode and solution rises until oxygen begins to be evolved and the solution becomes acid in the vicinity of the electrode. At the same time the layer of chloride near the bottom of the rod begins to turn white, and finally, as the electrolyte in the vicinity of the electrode becomes

[1] In McBain's compilation (see page 177 of this paper) incorrectly given as platinum anode.

[2] Noyes and Sammet, J. Am. Chem. Soc., **24**, 947 (1902).

exhausted, a white cloud of colloidal silver chloride is given off from the electrode and migrates downward with the current.

If the current density is increased, gaseous chlorine is also evolved at the electrode. Noyes and Sammet found that with a current density of not more than 4.5 milliamperes per square centimeter no chlorine was evolved, but the formation and migration of the cloud of silver chloride from the electrode was always obtained, as was also the liberation of oxygen and the formation of an equivalent amount of acid in the solution. In the analysis of their anode portion they were therefore obliged to dissolve the silver chloride from the anode by means of ammonia, and determine it along with the total chloride in the anode portion. This formation of acid can, however, be entirely prevented by using an electrode with a sufficiently large surface and taking precautions to prevent the exhaustion of the electrolyte in its immediate vicinity. At the same time a closely adherent layer of dark gray silver chloride is obtained, and the formation of the white colloid in the solution is entirely prevented. Two types of anodes were used in the present investigation. Type A, made from silver wire, is best adapted for use with dilute solutions, say from 0.2 molal down. For more concentrated solutions, a much larger surface of electrode must be available, and type B was devised to meet this requirement.

Preparation of Type A Anode.—This anode is made of No. 21 B. & S. gauge, pure silver wire (diameter 0.7 mm.), which is wound into a loose spindle about 3 cm. long and 2.2 cm. in diameter. In order to secure the necessary distance between the successive layers of the coil, each layer is separated from the preceding one by a few sheets of gun cotton, which is burned out after the coil is completed. The gun cotton is prepared by the nitration of an ashless filter paper in a mixture of three parts of concentrated sulphuric and one part of fuming nitric acid for forty-eight hours, followed by a thorough washing. When properly prepared, these gun cotton layers burn out readily, leaving an electrode with a large surface easily permeable by the solution in all its parts. After burning out the gun cotton, the electrode is plunged into warm dilute nitric acid until it is attacked violently, washed with boiling distilled water and then with alcohol, the excess of which is finally removed by ignition. This treatment removes the grease and dirt and imparts a matte surface to the wire, in which condition it is more readily attacked by the chlorine.

Preparation of Type B Anode.—A silver wire of suitable length is

wound into a flat spiral, the ends being brought up vertically through the centre of the spiral and twisted together to form the lēad wire. The spiral is placed in the bottom of a filter paper tube, as shown in the

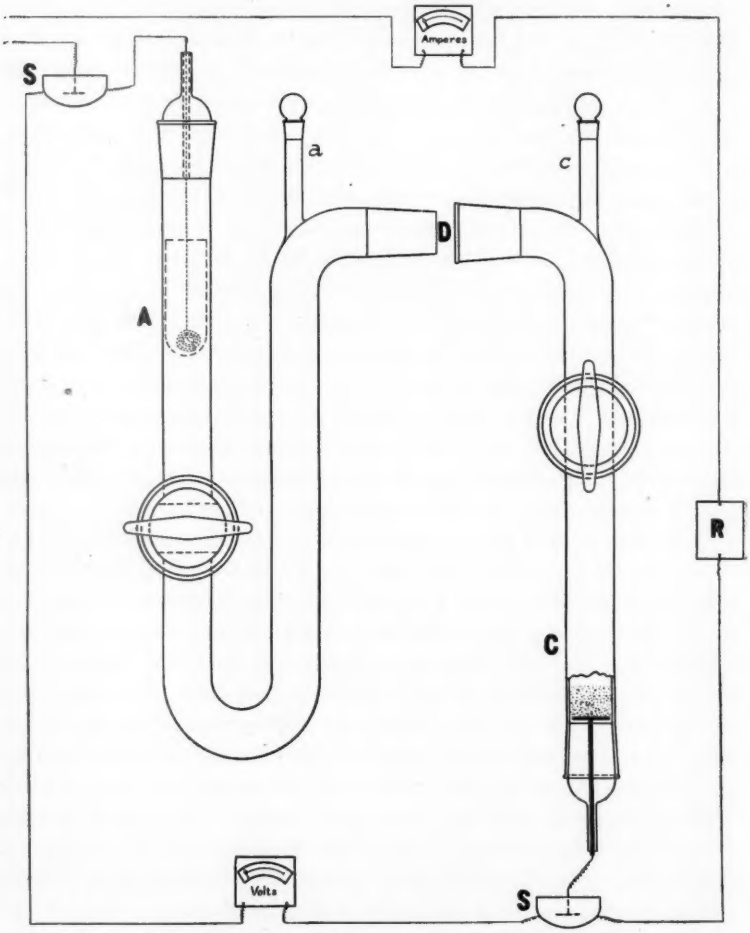

FIG. 1.—DIAGRAM OF APPARATUS AND CONNECTIONS

diagram (Fig. 1). The tubes used for this purpose are the familiar Soxhlet extraction cartridges, which can be purchased in several sizes. The size to be used depends upon the dimensions of the apparatus and

the amount of electricity to be sent through it. Those used in the present investigation were 6 cm. long and 1.9 cm. in diameter.

After the wire is in place, the cartridge is filled with "electrolytic crystals" of pure silver, which are packed tightly around the lēad wire. These crystals are prepared by the electrolysis of a silver nitrate solution with a silver anode and platinum cathode. The clusters of crystals so obtained are broken up somewhat and are then washed with hot water and finally with methyl alcohol, which is removed by ignition. The result is a mass of bright crystals of pure silver, which when packed in the cartridge as described give a silver electrode of maximum surface in the minimum volume. When the electrode is prepared, the filter paper cartridge is punctured with numerous needle holes to ensure ready penetration of the solution throughout the mass of silver. This form of electrode has been found to be eminently satisfactory. All of the silver surface is available as electrode, the crystals being changed to silver chloride without losing their form or porosity. Moreover, the electrode is easily broken up and mixed with the anode portion when the electrolysis is completed. An electrode of the above dimensions will carry a current of 0.1 ampere for sixteen hours without the formation of the slightest trace of acid or of colloidal silver chloride in the solution.

Preparation of the Silver Chloride Cathode.—This electrode consists essentially of a silver disk covered with the necessary amount of granular silver chloride. The disk is of such a diameter as to just slip into the apparatus tube. A silver rod welded into its centre passes out through the stopper of the apparatus, where it is joined to the lēad wire, as shown in the diagram. The disk is first cleaned by plunging it into warm nitric acid and is then suspended in a normal sodium chloride solution in a U-tube. Using it as an anode, a current of 0.025 ampere is passed through the solution until gas is evolved freely at the anode. The electrode is then removed, washed thoroughly with hot water and dried. The rod is then drawn through the opening in the stopper of the apparatus and cemented firmly in place, after which the stopper is inserted in the apparatus and a suspension of silver chloride is poured in until a column of the desired thickness is formed upon the electrode.

The silver chloride for this purpose is prepared by precipitating a hot solution of silver nitrate with an excess of an alkali chloride solution and washing thoroughly with boiling water. The precipitate is then washed by decantation with the stock solution of the alkali chloride

under investigation, until the liquid in contact with it has the same composition as the stock solution. This mixture is then poured upon the cathode by means of a thistle tube reaching nearly to the bottom of the cathode half of the apparatus. After the silver chloride has settled, the supernatant liquid is pipetted off, and after filling the apparatus the electrode is ready for use. During the passage of the current the silver chloride is reduced to gray metallic silver. It is only necessary to keep the current density low enough so that the rate of solution of the silver chloride is sufficiently rapid to supply the necessary amount of silver ion to carry the current from solution to electrode. An electrode 2.3 cm. in diameter will carry 0.5 ampere without the evolution of hydrogen or the formation of the slightest trace of alkali. It has been found that the physical condition of the silver chloride plays an important part in this action. If it is prepared by precipitation in the cold, it fails to act as a depolarizer. Boiling the precipitate seems to affect its physical condition so as to render it more soluble or more easily reduced. It should, of course, be protected from the action of white light.

III. The Apparatus

It is very desirable that the apparatus for transference experiments be as simple in form as is consistent with its main requirement, which is to secure the maximum transport of electrolyte and the maximum concentration change at the electrodes. The chief disturbing element is the mixing of the solution around the electrode with the rest of the solution. This may be caused by diffusion, by convection due to heat developed by the current, or by currents set up when the different portions of the solution are separated from one another at the end of the experiment.

The form of apparatus[1] finally adopted is designed to reduce these effects to a minimum. It is a modified form of the apparatus used by A. A. Noyes in his investigation of the transference numbers of the alkaline-earth metals.[2] It is shown in Figure 1. The anode tube, *A*,

[1] The apparatus designed for this investigation was constructed by Mr. Otto Pressler, of Leipzig, under the direction of Dr. W. Böttger, who was a Research Associate in this laboratory at the time this investigation was begun (1904–05), and who kindly offered to superintend the construction of the apparatus for me upon his return to Leipzig the following year. The construction of the apparatus offered considerable difficulty at first, owing chiefly to the size of the stopcocks, and I gladly take this opportunity to express my indebtedness to Dr. Böttger, to whose kindness and friendly interest is largely due the final construction of a satisfactory apparatus.

[2] Noyes, J. Am. Chem. Soc., **24**, 946 (1902).

is a U-tube having the top of its shorter arm bent at right angles and fitted by means of a ground glass joint, *D*, into the corresponding portion of the cathode tube, *C*. The short tubes, *a* and *c*, are provided with glass stoppers and serve to admit the stem of a pipette for the removal of the solution. The top of the anode tube *A* is fitted with a ground glass stopper carrying a small tube sealed through its centre for the admission of the lēad wire to the anode. The bottom of the cathode tube *C* is provided with a similar stopper. As soon as the cathode disk has been prepared as directed above, its lēad wire is sealed into the small tube with Khotinsky cement and the stopper is then sealed in place with the same cement.

The two large stopcocks serve to cut off the two electrode portions when the electrolysis is finished. The *whole* apparatus is of uniform bore (2.3 cm. diameter) throughout, including the cross tubes of the stopcocks. This is essential in order to prevent local heating and consequent stirring during the passage of the current. The apparatus is kept in a water thermostat at constant temperature during the passage of the current. The keys of the two stopcocks are hollow, the rear face of each being cut off so that the water of the thermostat can circulate about the cross tube. Apparatus and support are shown in the photograph, Fig. 2.

IV. Procedure of a Transference Experiment

Setting up the Apparatus.—The apparatus is cleaned thoroughly with warm chromic acid solution, and after washing with water and drying with pure alcohol the two tubes are placed in their supports, as shown in the photograph. Each stopcock is slightly greased with vaseline, the surface immediately opposite the cross tube being, however, left free from vaseline, so that on closing the cock the lubricant will not come in contact with the solution in the apparatus. After the insertion and alignment of the stopcocks, a thin layer of melted paraffin is applied by means of a camel's-hair brush to the joint between the key and the sheath, both front and rear. This paraffin seal entirely prevents all connection between the solution in the apparatus and the water of the thermostat, and at the same time allows the cock to be turned easily.

After the insertion of the electrodes the two halves of the apparatus are joined at the ground glass joint, which is also lubricated with vase-

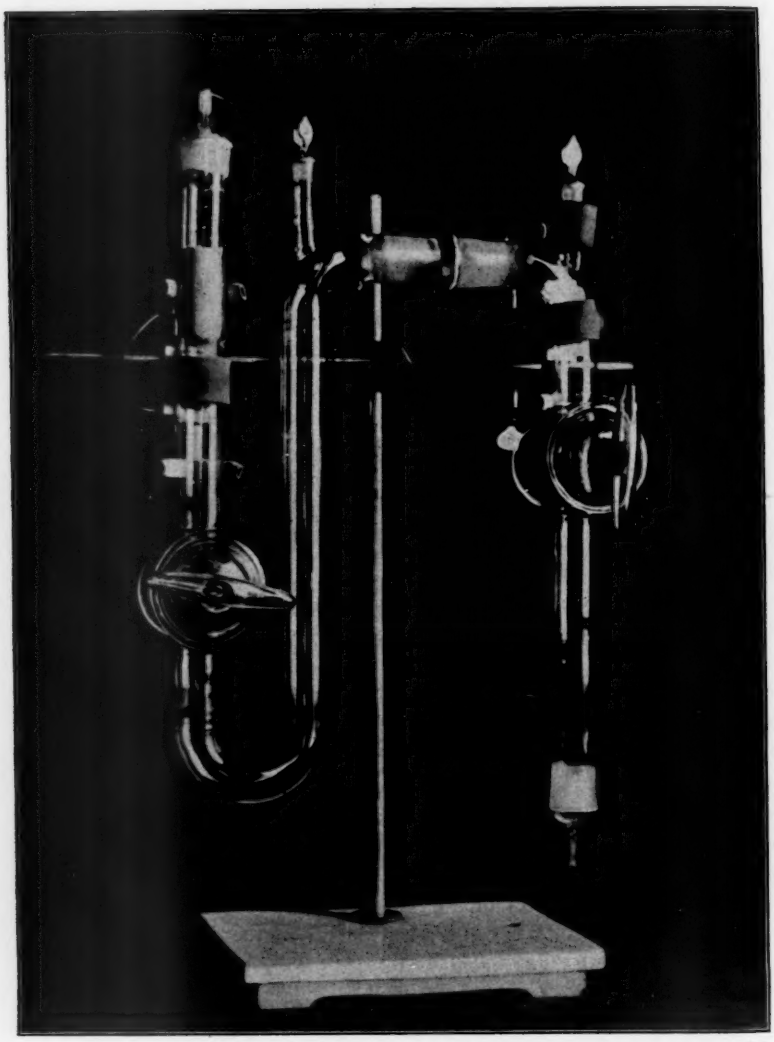

FIG. 2.—PHOTOGRAPH OF APPARATUS AND STAND

line[1] and protected with the paraffin seal in the same manner as the stopcocks. The lēad wires from the electrodes are protected from the water of the thermostat by rubber tubes which are brought out through rubber bushings in the side of the thermostat and the wires connected to binding posts. As a further precaution a piece of rubber band tubing is drawn over the bottom of the cathode tube as far as the stopper, and is then brought up above the surface of the water.

After filling the apparatus with the stock solution, the anode is moved up and down a few times to remove air bubbles, and is then fixed so as to occupy a position about three centimeters above the stopcock. This arrangement leaves considerable solution above the electrode, which stirs slowly during the run and prevents the exhaustion of the electrolyte in the immediate vicinity of the electrode. The three glass stoppers at the top of the apparatus are sealed with the paraffin seal, and the whole apparatus is placed in the thermostat to such a depth that the water and the solution in the tube are at the same level.

The connections are made as shown in the diagram. Two silver coulometers, *S*, one connected to the anode and the other to the cathode, serve to detect any leakage during the passage of the current. After the solution has come to the temperature of the thermostat, the circuit is closed and the rheostat, *R*, adjusted to the proper current strength. The voltmeter which is connected in shunt just outside the coulometers serves to indicate the progress of the electrolysis. During the first hour or two the potential across the apparatus gradually falls to a value which remains constant until near the end of the run, when it begins to rise gradually. This increase begins when the whole surface of the anode is covered with the chloride layer. When the potential has risen one volt, the circuit must be broken or oxygen will be evolved at the anode.

Removal of the Solution.—As soon as the circuit is broken the two stopcocks are closed, and by introducing a pipette into the apparatus through the small tube on the cathode side the solution is drawn out of the horizontal portion of the tube and down to the cathode stopcock. This portion, which will be called the cathode middle portion (M_c), is transferred to a 150 c.c. glass-stoppered, tared, Erlenmeyer flask. In a similar manner two other portions are removed; the middle portion (M), which extends down to the bend in the anode tube, and the anode middle portion (M_a), which comprises the rest of the solution around to the anode stopcock.

[1] The vaseline used for lubrication should be freed from all soluble matter by repeated extraction with boiling water.

After the removal of these portions the apparatus is taken from the thermostat, dried on the outside, the rubber tubes removed, and the cathode lēad wire disconnected. The two halves of the apparatus are disconnected at the ground glass joint and paraffined rubber stoppers are inserted in each. After first opening the stopcock, the contents of the cathode tube are mixed thoroughly, and then after sealing all joints with paraffin it is set aside to allow the silver and silver chloride to settle out. The anode stopcock is opened and the anode lowered until it can be caught between the stopcock and the wall of the tube. In this manner it can be broken up and mixed with the solution. After thorough mixing, this half of the apparatus is also sealed with paraffin and set aside to allow the silver chloride and filter paper shreds to settle.

Each half of the apparatus is cleaned and dried on the outside and weighed to the nearest centigram. The bulk of the clear solution is removed with a pipette and transferred to a small, glass-stoppered Erlenmeyer flask. The residue from the electrode is washed out into a beaker, and after drying the empty apparatus with alcohol and ether it is weighed. The electrode residue of silver and silver chloride is collected on a filter, washed with alcohol and ether, dried and weighed. The necessary data for calculating the total weight of the electrode portion are thus obtained.

V. The Coulometers

The silver coulometers used in this investigation were of the ordinary type, the cathode consisting of a platinum disk and the anode of a silver disk covered with a close filter paper. Guthe[1] has recently shown that the results obtained with this type do not differ by more than 0.05 per cent. from those obtained with the more accurate Richards type, a degree of accuracy which is amply sufficient for transference work. The silver nitrate solution for the coulometers was freshly prepared for each experiment.

VI. Experimental Results

To illustrate the character of the results which can be obtained with this apparatus, the data of two runs with 1.2 molal KCl solution are given in the accompanying table. The temperature of the thermo-

[1] Guthe, Bull. Bureau Stand's, 1, 28 (1904).

stat was maintained at 25° and the current strength at 0.1 ampere for twelve to fourteen hours, the drop of potential through the apparatus being 18 volts.

TABLE

	Run I.	Run II.
Ag deposited in coulometer (A)	5.0866	5.3685
Weight of electrode portion (A)	99.83	103.21
Percentage of KCl in portion (A)	6.790	6.510
Percentage of KCl in portion (M_a)	8.346	8.105
Percentage of KCl in portion (M)	8.348	8.108
Percentage of KCl in portion (M_c)	8.349	8.108
Percentage of KCl in portion (C)	10.168	10.03
Weight of electrode portion (C)	85.72	85.28
Ag deposited in coulometer (C)	5.0855	5.3681
Equivalents of electricity passed through	0.04713	0.04974
Grams of KCl transferred (A)	1.696	1.794
Grams of KCl transferred (C)	1.703	1.784
Therefore transference number of anion (A)	0.518	0.517
Therefore transference number of anion (C)	0.516	0.519

These results illustrate the exactness with which the two electrode portions can be cut off from the adjoining middle portions without any mixing. In most cases the changes in these middle portions are so small that no correction need be applied for them. It is essential that more than one middle portion be obtained and analyzed in transference work. If only a single middle portion be taken, it may be found on analysis to be practically unchanged, even though mixing has taken place with *both* electrode portions, since these two effects would tend to counterbalance each other. With three middle portions, however, all uncertainty on this point is removed.

The calculation of the transference numbers given in the above table was made in the usual manner. That is, the mass of solvent (m_s) in the electrode portion is multiplied by the ratio of electrolyte to solvent in the original solution, thus giving the mass of the electrolyte in m_s

grams of solvent before the electrolysis, whence by subtracting the mass of electrolyte in the electrode portion the amount of electrolyte transferred is obtained. The number of equivalents of electrolyte transferred, divided by the number of equivalents of electricity passed through the solution, gives the *ordinary transference number* of the anion, T_s^w. In this method of calculation the assumption must be made that the solvent is absolutely stationary, that is, that no transfer of solvent takes place from one electrode to the other. If such a transfer of solvent takes place, which would be the case if the ions were hydrated and carried water with them as they moved through the solution, the calculation of the transference number by the above method is not justified and will not give the *true transference number*, T_t. In fact, the number so obtained does not represent any physical quantity. Only in dilute solutions, where the amount of solvent transferred becomes negligible in comparison with the total solvent present, will the ordinary transference number T_s approach the true one, T_t. The measurement of the relative ionic hydrations and *true* transference numbers by means of this apparatus will be described in a future communication.

VII. Modification of the Apparatus for Use with Dilute Solutions

The procedure as described above is applicable only to comparatively concentrated solutions, say from 0.2 molal up. For more dilute solutions the apparatus is modified slightly in order to effect the necessary amount of transport of electrolyte and to provide a larger amount of solution for analysis. This is effected at the anode by increasing the length of the anode tube above the stopcock without, however, altering the position of the electrode, which in this case is type A. The increased amount of electrolyte above the anode stirs during the run, thus supplying the necessary amount of chloride ion for carrying the current to this electrode and allowing a corresponding greater transport to be obtained. It is better to obtain this increase in electrolyte by increasing the depth of solution above the electrode rather than by using an apparatus of larger cross section, since as the diameter of the tube increases it becomes more and more difficult to maintain a constant temperature throughout the tube and avoid the convection currents due to heating. At the cathode the increased volume is secured by an expansion of the tube for a short distance above the electrode. The same apparatus can

be employed for both concentrated and dilute solutions by having the two additional tubes ground to fit the same socket as the stoppers, so that they can be inserted when desired.

As an additional precaution against stirring, the use of diaphragms will be found advantageous for the more dilute solutions. These diaphragms, which are made of a medium-mesh silk bolting cloth, are conveniently inserted in the cross tubes of the stopcocks. The cloth is drawn over a thin vulcanite ring, which is then pressed into the cross tube of the stopcock, which it just fits. Hittorf[1] has shown that diaphragms of this character do not produce cataphoresis.

NOTE. — An excellent and exhaustive compilation and criticism of all transference work up to the end of 1905 will be found in a paper by J. W. McBain. [Proc. Wash. Acad. Sci., 9, 1 (1907)]. [Univ. Toronto Pub. No. 67.]

Boston, June 1, 1908.

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[1] Hittorf, Z. Phys. Chem., 39, 617 (1902).

DEMONSTRATION APPARATUS FOR ILLUSTRATING COMMUTATION[1]

By HARRISON W. SMITH

It is well known that sparkless commutation in direct-current machines occurs when the current in any armature coil, at the end of the period during which it is short-circuited by a brush, is equal in magnitude but opposite in direction to the current which was flowing in it at the beginning of short-circuit. In order that this may take place, the current which is flowing in the coil at the beginning of short-circuit must fall to zero, and a new current must be established in the reverse direction and equal, at the instant short-circuit ceases, to the initial current. The chief factor in accomplishing this reversal of current is the commutating E.M.F., which may be obtained by moving the brushes so that the coils are short-circuited in the proper "commutating field," or by furnishing the commutating field through the use of special commutating poles. A second important factor is the contact resistance of the brush when carbon brushes are employed.

For the purpose of illustrating these features of commutation two pieces of apparatus have been devised for use at the Massachusetts Institute of Technology. One shows how commutation with a low-resistance metallic brush is affected by the magnitude of the reversing E.M.F., by the self-inductance of the coil, by the magnitude of the current to be reversed, and by the time available for commutation. Another piece of apparatus shows how commutation is assisted by a brush of high contact resistance independent of all other factors.

Figure 1 is from a photograph of the apparatus for illustrating the features associated with commutating E.M.F., and Figure 2 is a diagram of its connections. Brushes B and B', built up of ¼-inch strips of brass, rest on a two-part commutator and convey a current from constant potential 230-volt mains. This current, which is to be reversed by the commutator C, may be varied in magnitude by the lamps L, L, L, L.

[1] Reprinted from The Electrician, January 17, 1908.

From the commutator C the current is taken by slip-rings through a coil, H, wound on a laminated iron core with a variable air-gap for the purpose of giving variable inductance, this coil obviously representing one of the coils on an armature as far as the reversal of current through it is concerned. In series with this coil is a double-throw switch, S, and the circuit is complete through the coil H alone when the switch is thrown to the left. Commutator C can be rotated by a small motor at speeds varying from 70 to 300 revolutions per minute. Brushes B and B', placed diametrically opposite, are each $\frac{3}{8}$ inch in width, while the gap

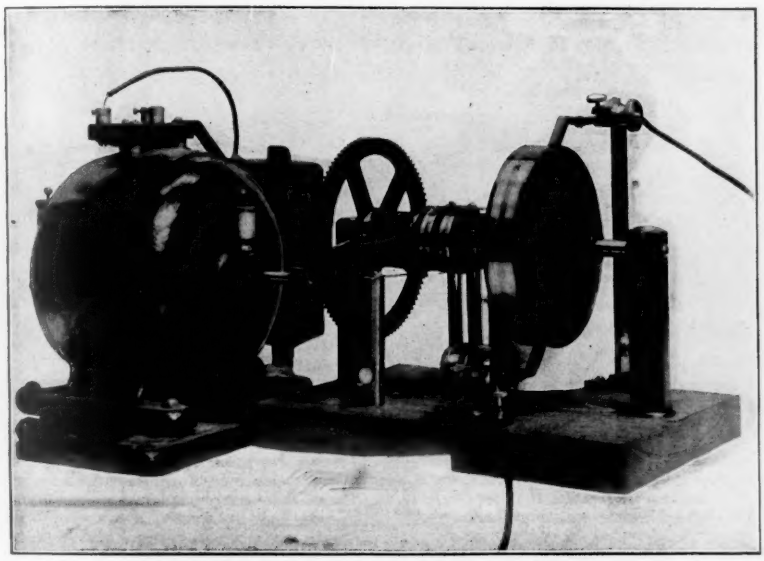

FIG. 1

between the segments of the commutator is $\frac{1}{8}$ inch. It is evident, then, that the segments of the commutator, and consequently coil H, will be short-circuited by both brushes simultaneously, and that short-circuit will cease at very nearly the same instant at both brushes. In fact, of course, slight irregularities in the edge of the segments will cause either brush B or B' to maintain short-circuit longer than the other, and whatever spark occurs will be seen at one brush only. It is desirable, therefore, to advance the upper brush B enough to cause short-circuit of the segments to cease always at brush B' just before the contact of B with the receding

segment is broken. In this way the process of commutation begins when B' short-circuits the segments and ends when B opens the circuit between itself and the receding segment. The advantage of this arrangement consists merely in having the spark occur at the upper brush, where it is most easily visible.

If, now, the switch S is closed to the left and the commutator caused to rotate, a spark will appear at B, the length of the spark being proportional approximately to the time necessary to build up the current in coil H.

In order to introduce an E.M.F. into the coil H the switch S is thrown to the right, the circuit of the coil then including an additional commutator, C', and a storage battery so arranged as to give an E.M.F.

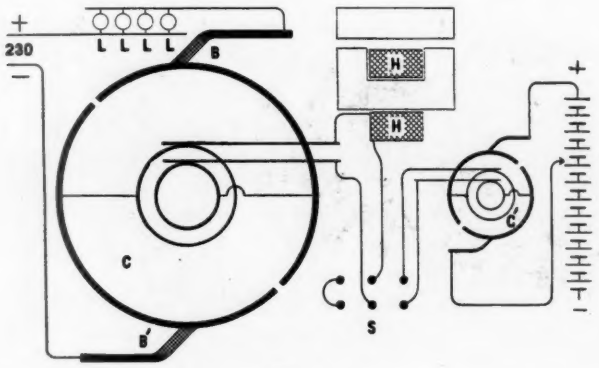

FIG. 2

variable from 2 to 24 volts. The commutator C' is placed on the same shaft with C, the two planes of commutation being normal to each other. As shown in Figure 2, the battery E.M.F. is evidently aiding the current in the coil, but after the commutator has rotated one quarter revolution it is evident that the battery E.M.F. will be opposing the flow of current through the coil. This connection of the battery with respect to coil H continues until after commutation has been effected, so that the battery E.M.F. will evidently assist in reversing the current in the coil as long as the segments of commutator C are short-circuited by brush B or B'. This battery, then, by the action of the commutator C', supplies an E.M.F. which acts precisely as the reversing E.M.F. in an ordinary armature.

The diameter of commutator C is 6 inches and of C' 2 inches. The coil H contains 300 turns of No. 12 Brown and Sharp gauge magnet wire wound on a laminated iron core 2.5 inches square.

A large number of experiments are at once suggested. Let the switch *S* be thrown to the left and a number of different brushes used successively at *B* varying in width from ⅜ inch to 1½ inches. Turn on lamps to give about 1.5 amperes from 230-volt mains. A spark will always occur, even with very low speeds, showing that no matter how wide the low-resistance brush be made, sparkless commutation cannot be obtained without a reversing E.M.F. Next, with the ⅜-inch brush at *B*, the commutator revolving about 70 revolutions per minute, the coil *H* adjusted for minimum inductance, and switch *S* thrown to the right, adjust the battery until no spark occurs. This will require about 6 volts. Either a larger or a smaller value of battery E.M.F. will cause sparks due to excessive or insufficient reversing E.M.F. Increase the current by turning on more lamps at *L*, and more battery E.M.F. must

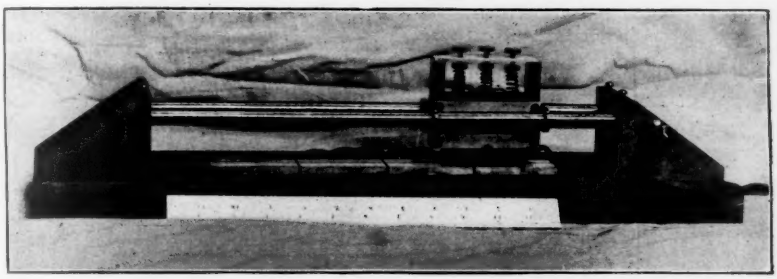

FIG. 3

be employed to prevent sparking. Next increase the inductance of *H*, which will require a larger reversing E.M.F., thus emphasizing the necessity of keeping down the inductance of armature coils. Again adjust the battery to give sparkless commutation, and substitute for the ⅜-inch brush the 1¼-inch brush without changing any other factors. A spark will now appear, due to excessive reversing E.M.F., and may be eliminated by reducing the reversing E.M.F., thus emphasizing the time element in commutation. Changing the speed of the commutator still further illustrates this feature. Let the speed of the commutator be increased, and sparks will appear which can be eliminated by reducing the inductance of *H*, by increasing the reversing E.M.F., or by using a wider brush.

In order to demonstrate the action of brush contact resistance in assisting commutation, the apparatus illustrated in Figure 3 is serviceable.

The electrical connections are shown in Figure 4, and this will at once be recognized as an adaptation of the method of discussion to be found in most treatises on the subject. Four brass plates, S_1, S_2, S_3, and S_4, representing four segments of a simple bipolar armature, are fastened to a slate base, and a carbon brush, B, can be drawn slowly across the segments, pressing firmly upon them.

Between the segments are placed three 5-ampere ammeters, having the zero point at the middle of the scale and representing three coils on the armature. The two paths through the armature are completed by two banks of lamps, L_1 and L_2, adjusted to take 5 amperes each from 115-volt constant potential mains. The currents from L_1 and L_2, after flowing into S_1 and S_4, respectively, unite in the brush B; and it is evi-

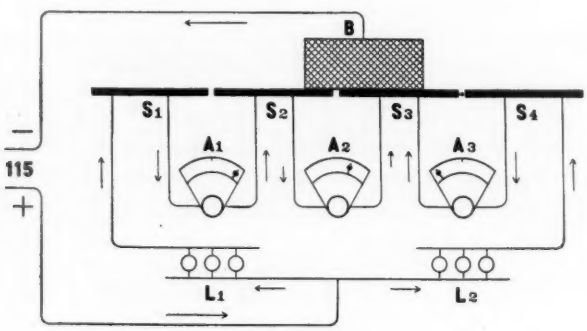

FIG. 4

dent that if B rested wholly on S_3 the current through A_1 and A_2 would flow from left to right, while the current through A_3 would flow in the opposite direction.

The diagram shows one-quarter of the brush resting on S_2 and three-quarters on S_3. If, then, the contact resistance of the brush is large compared with the resistance of the ammeter A_2, one-quarter of the current entering B, or 2.5 amperes, must flow from S_2; and since the current entering S_2 is 5 amperes, there must be 2.5 amperes flowing from S_2 into S_3. If it is considered that the brush is moving from right to left, it is evident that the current in A_2, which was 5 amperes when B rested wholly on S_3, has decreased to 2.5 amperes at the moment the brush is in the position shown, and that as the brush moves from the position where it rests wholly on S_3 to the position where it rests wholly

on S_2 the current in A_2 is gradually reversed. The arrows indicate in length the magnitude of the current in different portions of the circuit. It is evident that 1 ammeter would be sufficient, but the experiment is made more effective by drawing the brush across all four segments, starting at S_4, in order to show the successive reversal of current in adjacent coils. The brush is beveled so as to give a contact surface about ⅛ inch wide by 2½ inches long, in order to increase the contact resistance. The other dimensions are approximately indicated by a 1-foot scale resting beside the slate base in Figure 3.

SERVICE TEST ON THE STEAMSHIP GOVERNOR COBB[1]

(PARSON'S TURBINE)

By W. S. LELAND and H. A. EVERETT

The test on the steamship *Governor Cobb*, of the Eastern Steamship Company, was run by the Massachusetts Institute of Technology to provide thesis work for some of the graduates in the Department of Naval Architecture.

The test was run under service conditions on the regular trip of the *Cobb* from Boston to St. Johns, via Portland and Lubec. Observations began on passing Boston Light and were continued for twenty-six hours: for the boiler test continuously; for the engine test at favorable times.

All observations were plotted, which presents an interesting study of the results and makes simultaneous readings possible with a limited corps of observers. The close agreement of these curves is a good check on the accuracy of the observations.

Time has not permitted the preparation of a complete report, but merely a summary of that portion of the test run at full speed under the most favorable conditions.

The horse power was determined by means of the Denny and Johnson torsion meter belonging to the United States steamship *Chester*, which was loaned by the Bureau of Steam Engineering, United States Navy Department, through the courtesy of Admiral Charles W. Rae, Chief of the Bureau. The details of the loan were arranged by Benjamin C. Bryan, Lieutenant Commander U.S.N., who gave the matter his personal attention and accompanied our party on the test.

The torsion meter was set up in the engineering laboratory and a thorough working knowledge obtained by the use of experimental apparatus before installing the meter on board. Thirty-six feet on the side shafts, and 49 on the centre shaft between inductors, was the greatest length obtainable, which gave a meter reading of about .50 and .73, respectively, at full power.

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[1] Reprinted from Transactions of the Society of Naval Architects and Marine Engineers, 1907, 15, 117–120, plates 37–39. Copyrighted.

In computing the horse power, 1.506, based on an assumed torsional modulus of elasticity of 11,600,000, was used for the constant K in the formula:

$$\text{H.P.} = \frac{Kd^4rR}{CL},$$

in which d = diameter of shaft in inches (6⅜).
r = torsion meter reading.
R = revolutions per minute

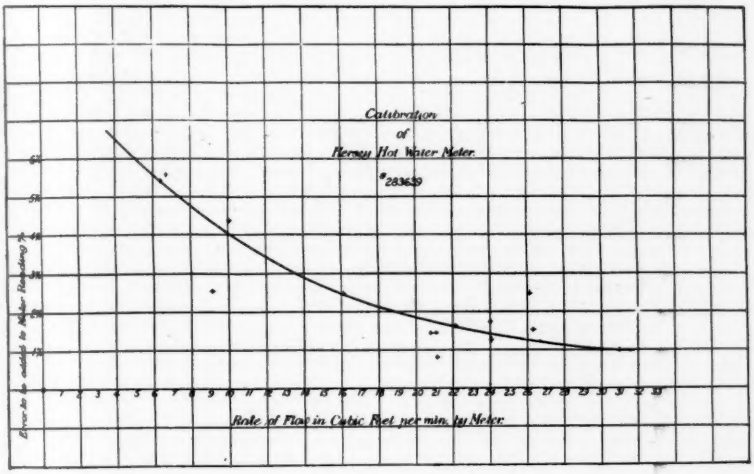
Calibration
of
Hersey Hot Water Meter
#283639
Error in % subtract to Meter Readings %
Rate of Flow in Cubic Feet per min. by Meter

FIG. 1

C = inductor constant (12.5).
L = length of shaft in feet between inductors.

The water consumption was measured by a Hersey hot water meter, loaned by the Hersey Manufacturing Company, of South Boston. It was installed in the suction line between the hot well and the feed pump, and gave exceedingly satisfactory results.

This meter was later calibrated under similar conditions, the curve in Figure 1 showing the percentages of error. The plot of meter readings was struck in as a straight line, showing practically a uniform rate of water consumption, no point varying from the line by a quantity greater than 1 per cent. of the total.

The steam for all auxiliary purposes was passed through the two

auxiliary lines, one on each side of the vessel, and the quantity measured by its flow through orifices. A thin steel plate, having a hole $1\frac{5}{16}$ inches in diameter, was inserted in each auxiliary line between two flanges near the boiler. Pressures were read simultaneously at both orifices and at no time showed a variation of over a pound after making the proper gauge corrections.

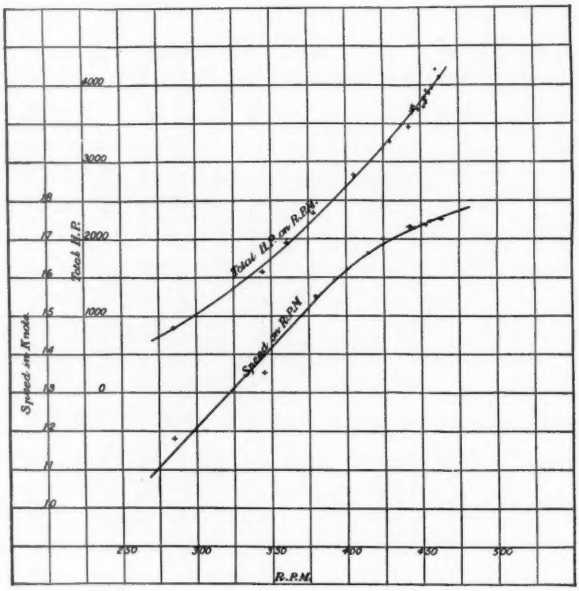

FIG. 2

The orifice was afterwards set up in the laboratory and its coefficient carefully determined by actually weighing the condensed steam under conditions similar to those on the boat.

Several buckets of coal were weighed, and their average, which varied only ten pounds from either maximum or minimum, multiplied by the number of buckets was taken as the coal consumption. The plot of coal consumption, like that of the water, is a perfectly straight line, showing a uniform rate.

The run from Boston to Portland was largely consumed in a progressive trial, the speed being taken by a stop-watch and a McGray electric

log towed from the end of a boom well clear of the wake. The log had previously been calibrated by towing over the measured mile.

Results of speed and power are shown in the curves in Figure 2.

The best run was made at full speed between Portland and Lubec, under the most favorable conditions of weather and sea. All observations were taken at ten-minute intervals excepting the coal, which was

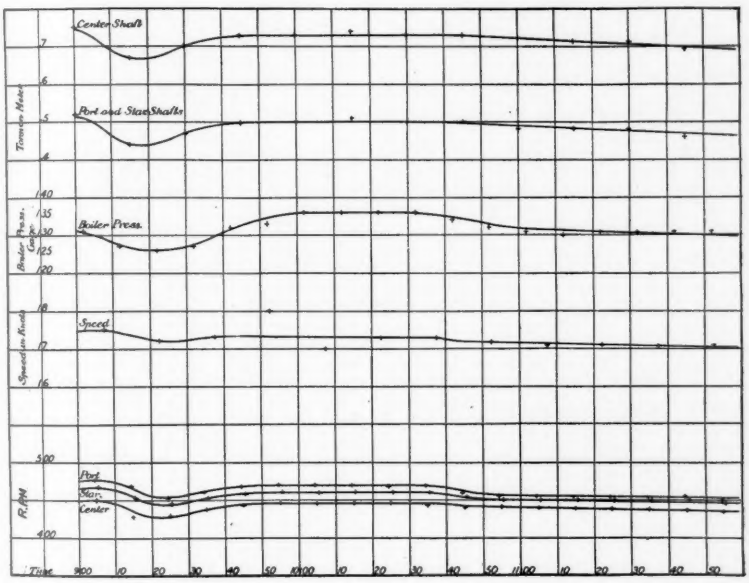

FIG. 3

recorded every fifteen minutes. Figure 3 shows the chief records during this test.

An attempt was made to determine the quality of steam, but as there were objections to tapping the main pipe a sample was taken from the drip connection which showed 2.5 per cent. of moisture, which is more than would be obtained from a fair sample.

It may be of interest to compare the following tabulated results with similar results obtained from a test on the steamship *Nantucket*, of the Merchants' and Miners' Transportation Company.

RESULTS OF TEST

	Nantucket.	*Cobb.*
Type of engine	Reciprocating	Parson's Turbine
Date of test	February 7, 1904	April 18, 1907
Duration of test — boiler	20½ hrs.	8 hrs.
Duration of test — engine	20½ hrs.	4 hrs.
Boiler pressure (average gauge)	147.3 lbs.	128 lbs.
Vacuum in inches	25	27
Quality of steam (sampled at drip)	98.8	97.3
Barometer	14.7 lbs.	14.7 lbs.
Temperature of air pump discharge	. .	110° F.
Temperature of feed water	209°.4 F.	213° F.
Kind of coal used	Georges Creek	Cape Breton
Moisture in coal	2.0%	1.9%
Ash and clinker in coal	7.6%	6.8%
Draft at blowers	Natural	2.1 in.
Number of boilers (single-ended Scotch)	4	6
Total grate surface	320 sq. ft.	323 sq. ft.
Total heating surface, approximately	10,150 sq. ft.	12,000 sq. ft.
Coal fired per hour	5,135 lbs.	8,050 lbs.
Water fed per hour (average during engine test),	45,844 lbs.	85,710 lbs.
Coal burned per square foot grate surface	16 lbs.	24.64 lbs.
Maximum revolutions	. .	p. 475, S. 460, C. 450
Corresponding total shaft horse power	. .	4,100
Average revolutions	74.05	447
Average total horse power	2,362 I. H. P.	3,747 S. H. P.
Steam for auxiliaries	. .	38,360 lbs.
Steam per I. H. P. per hour, total	19.41 lbs.	. .
Steam per shaft horse power per hour for all purposes	. .	22.67
Steam per shaft horse power per hour (propelling machinery only)	. .	19.74 lbs.
Speed (average)	15.00 k.	17.21 k.

DIMENSIONS

	Nantucket.	*Cobb.*
Length between perpendiculars	274 ft.	290 ft.
Beam molded	42 ft.	51 ft.
Draught	15 ft.	13 ft.
Displacement	2,700 tons	. .

ON THE FREE ENERGY OF NICKEL CHLORIDE[1]

By M. de Kay Thompson and M. W. Sage

I. Introduction

In a previous paper[2] by one of the authors, calculations of the free energy have been made, from potential measurements, of all compounds for which the necessary data already existed, but so far no direct free energy determinations of salts have been made on the principle underlying these computations. The object of the following investigation is to determine the free energy of nickel chloride by this method, for a full description of which reference may be made to the above paper. Briefly, for the salt here investigated it consists in measuring the electromotive force of the cell:

$$\text{Nickel} \mid \text{Saturated solution of } NiCl_2 \mid Pt + Cl_2.$$

If the salt contained no water of crystallization and the chlorine were at a pressure of 76 cm. of mercury, the free energy increase of one mol of the salt would be,

$$\Delta F = -2EF$$

where E is the measured electromotive force and F is one faraday.[3] On account of the fact, however, that nickel chloride takes on water of crystallization, a slight modification of the ideal process by which the nickel and chlorine are allowed to unite reversibly is necessary.

Nickel chloride, in contact with water, forms the hydrate $NiCl_2.6H_2O$.[4] A hydrate with four mols has also been detected,[5] but this existed in contact with a saturated solution at a temperature about 80°, and conse-

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[1] Reprinted from the Journal of the American Chemical Society, 30, No. 5. May, 1908.

[2] Jour. Am. Chem. Soc., 28, 731 (1906).

[3] To bring the conception of free energy increase into conformity with the present more general usage, the terms involving RT are included in ΔF. See Haber, Thermodynamik technischer Gasreaktionen, p. 9.

[4] Lescœur, Ann. chim. phys. [6], 19, 533 (1890).

[5] Etard, *Ibid.* [7], 2, 545 (1894).

quently would not enter into this process. According to Lescœur, the anhydrous salt is produced directly on dehydrating that with two mols of water. This conclusion is based on vapor pressure measurements at 100°, starting with $NiCl_2.2H_2O$ and making measurements after successive evacuations of the apparatus. The final analysis of the hydrate gave $NiCl_2.1.45H_2O$, which might be a mixture of $NiCl_2.2H_2O - NiCl_2.1H_2O$ or $NiCl_2.2H_2O - NiCl_2$. Although this point is doubtful, it will be assumed that there is no hydrate with one mol of water.

The salt in contact with the saturated solution of nickel chloride is then $NiCl_2.6H_2O$, and in the ideal process, as nickel and chlorine unite and precipitate from the solution, water would be removed from the solution, and in order to keep the amount of water in the solution constant, this has to be supplied reversibly and isothermally at the same rate at which it is removed. This may be accomplished by means of isothermal distillation, as follows: Consider water at the temperature in question enclosed in a cylinder with a frictionless piston. Allow six mols to evaporate reversibly and isothermally. The free energy increase of the system is $-6RT$. Now separate the six mols and allow them to expand reversibly and isothermally until the pressure is equal to the vapor pressure of a saturated solution of $NiCl_2.6H_2O$. The free energy increase of the system in expansion is

$$-6RT\log\frac{p_{H_2O}}{p_{sol}},$$

if p_{H_2O} is the vapor pressure of water at T° absolute and p_{sol} is the vapor pressure of the solution. The water vapor may now be condensed reversibly into the solution at the same rate at which it is removed by the salt crystallizing out. The free energy increase of the system in this last step is $+6RT$, so that the net result is the free energy increase, $-6RT\log\frac{p_{H_2O}}{p_{sol}}$.

$$\Delta F_1 = -2E_F - 6RT\log\frac{p_{H_2O}}{p_{sol}} \qquad (1)$$

is, therefore, the free energy of $NiCl_2.6H_2O$ referred to gaseous chlorine at atmospheric pressure and liquid water, both at T° absolute.

The free energy of $NiCl_2.2H_2O$ may be obtained from this by allowing $NiCl_2.6H_2O$ to change reversibly into $NiCl_2.2H_2O$ and four mols of liquid water. To do this allow four mols of water to evaporate

at the vapor pressure p_1 of the system $NiCl_2.6H_2O - NiCl_2.2H_2O$, whereby ΔF is $-4RT$. The water vapor must now be compressed to the vapor pressure p_{H_2O} of water, in which process ΔF is

$$+ 4RT \log \frac{p_{H_2O}}{p_1}.$$

The water vapor is then condensed to liquid water, in which ΔF is $+ 4RT$.

The free energy increase then of $NiCl_2.2H_2O$ is

$$\Delta F_2 = - 2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1}. \qquad (2)$$

By an exactly similar process the free energy increase caused by $NiCl_2.2H_2O$ going over to $NiCl_2$ and $2H_2O$ is

$$+ 2RT \log \frac{p_{H_2O}}{p_2},$$

where p_2 is the vapor pressure of the system $NiCl_2.2H_2O - NiCl_2$, and hence the free energy increase of formation of $NiCl_2$ is

$$\Delta F = - 2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1} +$$

$$2RT \log \frac{p_{H_2O}}{p_2} = - 2EF + RT \log \frac{(p_{sol})^6}{p_1^4 p^2} \qquad (3)$$

To all the above expressions a small correction must be made for the gaseous chlorine, whose pressure will, in general, not be 76 cm. of mercury. Assuming the vapor pressure of the solution to be unaffected by the presence of the chlorine in the enclosed space above, the chlorine couple[1] would be $b - p_{sol}$ where b = barometric pressure. The increase in free energy of the system when the chlorine expands from 76 cm. to $b - p_{sol}$ is

$$\Delta F = - RT \log \frac{760}{b - p_{sol}},$$

which must be added to the right-hand side of equation (3).

II. Potential Measurements

The apparatus in which the potential measurements were carried out consisted of an H-tube, 15 cm. high, with a glass stopcock in the

[1] See Jour. Am. Chem. Soc., **28**, 733.

horizontal arm. The tubes of the vertical arms were 2 to 3 cm. in diameter. The stopcock was not lubricated and the potential of the cell was usually measured with the stopcock turned off.

The chlorine electrode was a smooth sheet of platinum with 10 per cent. iridium, 10 cm. long by 3 cm. wide. This was half way immersed in the solution, and chlorine gas, generated by the electrolysis of strong hydrochloric acid, bubbled over it from below. The chlorine was led from the cell by a rubber tube to a bottle containing potassium hydroxide, where it was absorbed. The pressure of the gas over the chlorine electrode was determined by a small manometer in the escape tube and by the barometer reading. The nickel electrode was formed by electrolytic deposition of nickel on platinum or copper. It is known that nickel exists both in the active and passive states and that active nickel rapidly changes over to the passive state if exposed to the oxygen of the air. Pure nickel immersed in molal nickel sulphate gives about -0.2 volt,[1] while, according to Muthmann and Frauenberger,[2] active nickel has a potential of $+0.32$ volt. The nickel having this potential was prepared by electrolytic deposition on platinum "according to the directions for electro-analysis." This statement and that which follows later, according to which the solution used was neutral nickel sulphate and the impressed voltage 8 volts, are all the directions given for obtaining a nickel deposit giving the voltage quoted above. The first measurements of the nickel couple were attempts to reproduce this potential in a molal solution of neutral nickel sulphate. The measurements were made by the Poggendorf method with a Weston standard cell and Lippmann electrometer. The potential between the nickel sulphate and normal potassium chloride was eliminated by a saturated solution of potassium chloride or ammonium nitrate placed between the two.[3] The potential was measured within thirty seconds after plating. It was found that on electrolyzing a neutral sulphate solution at room temperature with 8 volts a green deposit appeared on the cathode whose potential was about that given by Muthmann and Frauenberger, and which decreased rapidly. On heating a solution containing 60 grams $NiCl_2.6H_2O$ per liter to 90° and electrolyzing with 12.5 volts, the nickel

[1] All single potentials in this paper refer to the "normal electrode" as -0.560 volt at 20°.

[2] Sitzungsber. kgl. Bayr. Akad. Wiss., **34**, 201 (1904).

[3] Bjerrum, Z. physik. Chem., **53**, 428 (1905).

came down in a black spongy form, and no green compound was visible. The highest potential obtained was $+0.112$ volt. Many other solutions were used, but none gave such high results as the neutral sulphate. For example, a solution containing 60 grams $NiSO_4.6H_2O$ + 20 grams $(NH_4)_2SO_4$ + 40 c.c. NH_4OH per liter, electrolyzed at 20° with 8 volts, gave a deposit of nickel whose potential was $+0.017$ volt. This was a gray, firm deposit, and could be easily duplicated. Our only explanation of Muthmann and Frauenberger's high value for nickel is that some of this green precipitate came down with the nickel. If this nickel was obtained in a cold solution with 8 volts, this is certain to have happened. The nickel deposits obtained in the hot solution did not maintain a constant voltage, but fell off as rapidly as in the case of the green precipitate obtained in the cold. Attempts to increase the voltage by polarizing with hydrogen were not successful. In preparing the nickel electrodes for the final measurements the anode and cathode were separated by the wall of a porcelain cup, and in all cases pure electrolytic nickel anodes were used. This cup was to protect the cathode from any sulphuric acid set free at the anode, as it was found, as stated by Muthmann and Frauenberger, that any free acid reduced the potential.

The actual measurement of the cell

$$\text{Nickel} \mid \text{Saturated solution } NiCl_2.6H_2O \mid Pt + Cl_2$$

at 20° was now taken up. A saturated solution of the chloride was prepared by rotating bottles for several days in a thermostat maintained at 20° by means of a mercury regulator and electric lamps. The dissolved nickel was determined by electro-analysis, and three determinations gave 60.5, 60.6, and 60.9 grams of anhydrous salt per hundred grams of water. This is somewhat less than 64 grams chloride to 100 grams water as found by Etard.[1] The density of this solution referred to water at 4° was 1.474.

Before making measurements, chlorine was allowed to bubble over the platinum-iridium plate for an hour or so, so as to give the solution in this arm of the H-tube time to get saturated with chlorine and to drive out all air above the solution. After leaving the cell it was tested by absorbing in potassium iodide in an inverted test tube. The absence of bubbles showed the gas to be pure chlorine. The electromotive force of this couple was measured against the "normal electrode" and was

[1] Landolt-Börnstein-Meyerhoffer Tables, 3d edition, p. 562.

found to be — 1.59 volts. The nickel electrode was now prepared as described above and changed from the plating solution to the cell as quickly as possible and the reading on the bridge taken immediately. This could be done within thirty seconds from the time the plating was finished. Cleaning off the sulphate adhering to the electrode by dipping in water did not affect the result. The electromotive force of the cell thus measured varied between 1.65 and 1.707 volts, the latter being the highest value obtained in a large number of measurements. This, therefore, corresponds to the most active nickel obtained above. The pressure of the chlorine gas at the time of the latter measurement was 752 mm. mercury.

As there is approximately 0.2 volt difference between the highest value here obtained and that which would have resulted if the nickel couples had as high a value as that assigned them by Muthmann and Freuenberger, some decomposition point determinations of the saturated solution between small platinum plates were made for the purpose of determining whether the above measured value is reversible. The values obtained were not used for computing the free energy, but were simply to decide whether an error of 0.2 volt in the above value were possible. The values found were 1.61, 1.63, 1.60, and 1.60 volts. These are somewhat less than the highest value found above, but the agreement indicates that 1.7 volts and not 1.9 volts is the voltage of the cell.

III. Vapor Pressures

The vapor pressure of the saturated solution of nickel chloride has been found by Lescœur[1] to be 8 mm. Hg and that of the system $NiCl_2.6H_2O$ — $NiCl_2.2H_2O$ to be 4.6 mm. Hg, both at 20°. The system $NiCl_2.2H_2O$ — $NiCl_2$ was found to have a vapor pressure at 100° of 123 mm. No measurement is given of this quantity at 20°, but the statement is made that it is zero, which is, of course, impossible.

By means of the integrated van't Hoff formula this pressure could be calculated, however, from the pressure at 100° if the heat of hydration of $NiCl_2.2H_2O$ were accurately known. This is equal to the difference between the heat of hydration of $NiCl_2.6H_2O$ starting from $NiCl_2$ and from $NiCl_2.2H_2O$. The former quantity is 20,330 cal.[2]

[1] Ann. chim. phys. [6], **19**, 533 (1890).

[2] Landolt-Börnstein-Meyerhoffer Tabellen, p. 461.

The following table shows the latter value, q, obtained from Lescœur's vapor pressure of the system $NiCl_2.6H_2O - NiCl.2H_2O$ by the formula:

$$4.57 \log_{10} \frac{p_2}{p_1} = q\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

All except the last column are taken from Lescœur.

Temperature.	Pressure in mm. Hg.	q.
15°	3.4	10,540
25°	6.3	
20°	4.6	14,760
30°	10.5	
40°	24.0	14,000
15°	3.4	
30°	10.5	15,470
40°	24.0	

Subtracting the average value of q from 20,330, the heat of hydration of $NiCl_2.2H_2O$ is obtained. Computing this from the value of the vapor pressure of $NiCl_2.2H_2O$ at 20°, 11.5 mm. results, which is greater than that of $NiCl_2.6H_2O$, and is therefore impossible. It is evident, therefore, that this value of the heat of hydration is not accurate enough for this purpose.

The value of this pressure was obtained directly by the tensimeter method. For this purpose one tensimeter was filled in June and three in July.[1] One bulb contained phosphorus pentoxide and the other the salt. The liquid in the manometer was cottonseed oil of specific gravity 0.9185. The tensimeters were placed on their side, carefully pumped out, and at the same time warmed. They were then left several hours in connection with the pump and again pumped out and warmed before sealing off. In October they were placed in a thermostat at 20° and allowed to remain until January. The following table gives the readings in millimeters of oil:

[1] See Findlay, The Phase Rule, p. 88.

Date.	No. 1.	No. 2.	No. 3.	No. 4.
December 30	11.4	7.0	3.6	5.4
January 7	. .	6.3	broken	6.4
January 25	11.6	6.8	. .	6.1
Mol water to 1 mol salt	2.06	2.05	. .	1.99

December 30, after the measurements, the bulbs of Nos. 2 and 5 containing the $NiCl_2$ were placed in a beaker of hot water for a few minutes to see if the evolution of water vapor could not be accelerated. The pressure increased to 10 to 15 cm. of oil, due, evidently, to the expansion of water vapor already present, but went back to nearly the same values afterwards. The water in the salt in the tensimeters was determined by analyzing for the amount of nickel present subsequent to these measurements, and the results were those shown in the table above. It is evident from the above that No. 1 was not properly filled, and is therefore omitted in taking the mean. The average of Nos. 2 and 4 is 0.43 mm. of mercury.

In order to check this value by a different method it was decided to measure it at 110° and compute by the van't Hoff equation from this and from Lescœur's value at 100°, the value at 20°.

For this purpose a tensimeter was filled with some nickel chloride that had been in the drying closet for more than a week at 100°. Mercury was used in the manometer and phosphorus pentoxide in the drying bulb. It was first placed in a steam bath to see that it checked with Lescœur's value. The tensimeter was left at four in the afternoon, and next morning was found at 123 mm. Hg, reduced to 0°, at which pressure it remained constant for the following twenty-four hours. This agrees identically with Lescœur's value. It was then placed in a bath of vapor from boiling toluene and in a few hours reached a constant pressure of 218 mm. Hg at a temperature of 110.7°, as obtained from a thermometer corrected at this point by a standard from the Reichsanstalt. The value at 20° computed from this is 0.46 mm.

The tensimeter was then opened and heated while exhausted and connected to the air pump for an hour and a half at a temperature varying from between 90° and 120°, thereby driving off some water. It was sealed off while hot and again placed in the bath of toluene vapor. The constant pressure reached as before in a few hours was

216 mm. Hg at 110.6°. The pressure computed from this measurement for 20° is 0.47 mm.

These values agree well enough for the present purpose with the average of those from direct measurements. The best value to adopt is the average of the four, which is 0.45 of mercury. It is interesting to note that on cooling, the mercury in the tensimeter immediately goes back to nearly a zero pressure, showing that water is taken up by the chloride more rapidly than it is evolved.

Substituting in formula (3) $E = 1.71$ volts, $p_{sol} = 8.0$, $p_1 = 4.6$, and $p_2 = 0.45$, $\Delta F = -74{,}400$ cal. The correction due to the pressure of the chlorine not being 760 mm. is negligible.

The heat of the reaction, or the increase in total energy, is $-74{,}500$ cal., assuming the compound to be formed from gaseous chlorine. If the chlorine were solid and superheated to this temperature, the total energy increase is obtained by increasing the above value by the sum of the heat of fusion and the heat of vaporization of chlorine, which has been estimated at 7,000 cal.[1] This gives $-67{,}500$ cal. as the total energy change, starting with solid chlorine. Likewise, if the chlorine were solid the free energy increase ΔF would be diminished by the quantity RT, or approximately 600 cal., giving the value $F = -75{,}000$. The ratio of free to total energy for chlorine in the solid state consequently is 1.11, while the ratio of the same quantities with chlorine in the gaseous state is 1.00. The free energy and the total energy of this salt, therefore, are approximately equal, as was found to be true in all other cases for which this calculation has been made.

IV. Precision Discussion

The term $2EF$ in formula (3) amounts to 79,040 cal., the second term to only 4,600 cal., from which it is evident that even a large error in the vapor pressures would have only a relatively small effect on the final result. Assuming an error of 0.1 mm. in p_{sol}, p_2 and 0.1 mm. in p, which seems an outside limit, the resultant effect is 600 cal., or about 0.8 per cent. error in ΔF. Assuming a possible error of 0.02 volt in E the combined error in ΔF would be 990 cal., or 1.3 per cent.

[1] Jour. Am. Chem. Soc., **28**, 741 (1906).

V. Summary

The free energy ΔF of $NiCl_2$ was determined by measuring the potential of the cell.

$$Ni \mid \text{Saturated solution of } NiCl_2.6H_2O \mid Cl_2 + Pt.$$

A formula for ΔF was deduced, involving this potential, the vapor pressure of the saturated solution of the system $NiCl_2.6H_2O - NiCl_2.2H_2O$ and of $NiCl_2.2H_2O - NiCl_2$. The pressure of the last system was obtained both by direct and by indirect measurement. The free energy and total energy of $NiCl_2$ were found to be approximately equal.

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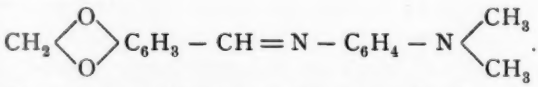
THE COLORED SALTS OF SCHIFF'S BASES—A CONTRIBUTION TO OUR KNOWLEDGE OF COLOR AS RELATED TO CHEMICAL CONSTITUTION[1]

By F. J. MOORE and R. D. GALE

Received January 6, 1908

I. The Hydrochlorides of Bases Formed by Condensing *p*-Amino Dimethylaniline with Aromatic Aldehydes

The starting point of the present investigation was a chance observation made upon the compound produced by condensing *p*-aminodimethylaniline with piperonal. This product is of a light orange color and has the formula,



When this substance, either in the dry state or in ethereal or benzene solution, is treated with dry hydrochloric acid gas, one molecule of the latter is first added to form a salt of a deep blood-red color. This salt can further add another molecule of the acid to form a dihydrochloride. The color of the latter salt, in sharp contrast to that of the former, is a bright lemon-yellow.

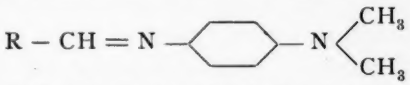
We found this phenomenon so striking that we determined to prepare a number of compounds of analogous constitution and study the color of their salts. The first substances selected were those most strictly analogous to the one already mentioned, namely, the condensation products of *p*-aminodimethylaniline with aromatic aldehydes. These bases furnish the subject-matter of the present paper. They all show a behavior toward hydrochloric acid, and (so far as has been tested) also toward other acids, entirely analogous to that described in the case of the piperonal compound. A minor exception has to be noted in the case of anisaldehyde. When its condensation product with *p*-aminodimethylaniline is treated with hydrochloric acid, the same color changes are observed as in the other cases, but analysis of the products shows

[1] Reprinted from the Journal of the American Chemical Society, 30, No. 3, March, 1908.

that a maximum of nearly three molecules of the acid is here absorbed. This behavior will be discussed more fully in the experimental part.

Subsequent papers will deal with other compounds similarly constituted. Thus we have prepared a number of bases of this class by condensing aromatic aldehydes with *p*-aminodiethylaniline. Of these it may be said that as far as investigated they show the same reactions toward acids as the corresponding dimethyl compounds. The salts are, however, less stable. One of us, in collaboration with Mr. R. G. Woodbridge, Jr., is also studying the bases formed by condensing *p*-aminodiphenylamine with aldehydes.

From the above it is clear that we are dealing with a quite general law, which may be stated thus: Bases of the general formula,



add hydrochloric acid to form salts of a dark red color (darker than that of the free base), while most of them also add another molecule of the acid to form salts of a light yellow color (usually lighter than that of the free base).

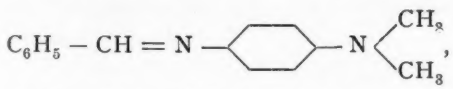
Before attempting a theoretical explanation of this uniform behavior, a word should be said concerning the color of the simpler benzylidene compounds containing only one atom of nitrogen. As aromatic aldehydes condense so readily with primary amines, a voluminous literature has grown up on the subject. We have not made an exhaustive study of this, but the general rule seems to be that neither such bases nor their salts are very highly colored. This certainly holds true of those which have come under our observation. Thus the condensation product of benzaldehyde with aniline is a pale cream color (perhaps due to a trace of impurity), and the product formed by treating piperonal with aniline is perfectly colorless. The hydrochloride of the piperonal compound is a bright lemon-yellow; that of the benzaldehyde compound a much paler shade, only slightly stronger than that of the free base. For purposes of comparison we have prepared several other condensation products of piperonal. All of these, namely, the compounds prepared by treating piperonal with *p*-toluidine, *p*-chloraniline, *p*-bromaniline, *p*-aminoethylbenzoate, and *m*-nitraniline, all showed the same light color of base and salt.

From this we can draw the conclusion that if the group $-CH=N-$ is to be considered a chromophore at all, it is a weak one; certainly far

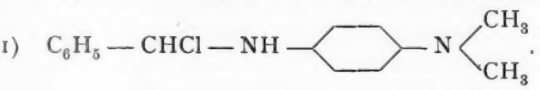
weaker than $-N=N-$. Of the intensifying effect of acid addition or salt formation, whether we call it "auxochrome" effect or "halochromy," we may say that in this group of compounds it is noticeable but not striking.

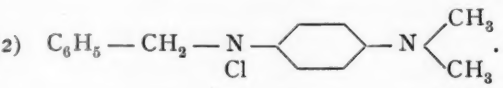
Turning back now to the more complicated bases containing two atoms of nitrogen, inspection of their formulæ shows the presence of the substituted amino group, $-N\langle^{CH_3}_{CH_3}$, which acts as an auxochrome in so many important dyes. The effect of this group is seen in the color of the bases which contain it. These colors range from a light yellow, through golden yellow, to a fairly strong orange. None go as far as deep red. The color of the salts has already been dwelt upon.

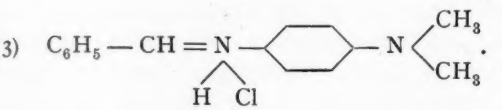
Our interpretation of the color relations so frequently referred to will depend upon our idea of exactly what happens when one molecule of hydrochloric acid is added to these bases. If we take for purposes of illustration the simplest case, that of benzylidene *p*-aminodimethylaniline,

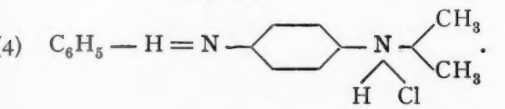


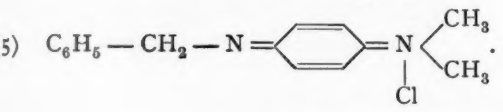
we can imagine hydrochloric acid being added to the compound in such different ways as to form products of any one of the following formulæ:

(1) 

(2) 

(3) 

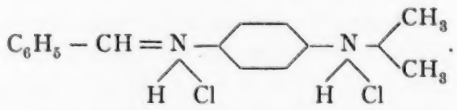
(4) 

(5) 

Of these, (1) and (2) seem hardly worthy of serious consideration. The addition products of acids to the simpler bases of this type, such as benzylidene aniline, $C_6H_5 - CH = N - C_6H_5$, have always been looked upon as ammonium salts. They split at once under the influence of water into the corresponding aldehyde and the salt of the base from which they were originally formed — in this case, aniline hydrochloride and benzaldehyde. The salts of the more complicated compounds now under discussion act in a similar way. This would exclude (1). It would not necessarily exclude (2), according to which the addition products are to be looked upon as secondary chloramines. They are, however, rather more stable than chloramines would be expected to be, and they do not evolve chlorine when they are treated with hydrochloric acid. A more conclusive argument, however, against (1) and (2), and in favor of the salt-like character of the compounds, is the fact that so far as tested (and only qualitative tests have thus far been made) sulphuric acid gives addition products entirely similar in color and properties to those formed by hydrochloric acid.

Formulæ (3) and (4) represent more nearly what we should expect if the addition of hydrochloric acid is to be looked upon as simple salt formation. The formulæ differ only in the nitrogen atom, which is supposed to become pentavalent. In deciding between them we have to remember that the simpler bases, like piperonylidene aniline, add one molecule of hydrochloric acid to form salts which are not dark red but light yellow. Now these salts must have their hydrochloric acid united to that nitrogen which forms part of the chain connecting the two benzene rings. It would therefore seem quite probable that these red salts have their hydrochloric acid bound differently. Furthermore, if we assign to the red salt the formula (4), a consistent and plausible explanation lies near at hand for the difference in color between the salts containing one and two molecules of hydrochloric acid, respectively. In the first case, we have three factors coöperating to intensify the color, the chromophore group, $- CH = N -$, the auxochrome group, $N\begin{smallmatrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{smallmatrix}$, and, finally, whatever influence in this direction is to be ascribed to salt formation — "halochromy."

Now the compound with two molecules of hydrochloric acid can hardly have any other formula than the following:



Here the nitrogen belonging to the chromophore group, $-CH=N-$, has changed its valence, and this might naturally be expected to prove destructive to the chromophore character of the group. Furthermore, the light yellow color of these saturated salts is in entire harmony with the similar color of the simpler bases which, as already pointed out, must have the hydrochloric acid upon the central nitrogen.

An argument against the explanation just outlined might be found in the hydrolysis of the salts. It is a well-known fact that the salts of the simpler bases, like benzylidene aniline, decompose at once when treated with water, yielding in this case aniline hydrochloride and benzaldehyde. The salts of the more complicated bases we are studying react similarly, except that the operation takes place in two steps. If the yellow hydrochloride of piperonylidene *p*-aminodimethylaniline, for example, be treated with water, it immediately turns dark red, obviously owing to the formation of the red monohydrochloride. The color then slowly fades out as this salt splits into the hydrochloride of *p*-aminodimethylaniline and piperonal. Now the weak spot in the hydrochloride of piperonylidene aniline is obviously the molecule of acid attached to the central nitrogen. If the red salt has then a constitution analogous to that shown in formula (4), it is not, at first sight, quite clear why it should hydrolyze at all. The above argument, however, against (4) does not seem as serious as that which can be brought against (3). If we give the latter formula to the red hydrochloride, we can only ascribe the intensity of its color to salt formation — halochromy. We should then expect a further intensification of the color when the second molecule of hydrochloric acid is added. As we have already seen, this is not the case.

There remains the quinoid formula, (5). This also offers a consistent explanation. We have only to assume that the red hydrochloride exists in the quinoid, the yellow dihydrochloride in the benzoid form. It seems at first a little difficult to account for the hydrolysis into aldehyde and amine salt on this basis, but the shifting of double bonds involved is not of a particularly revolutionary character. It would also seem possible that the dihydrochlorides might also exist in a quinoid form. Perhaps when more compounds have been studied such salts

will be found. In the meantime, some work is under way in this laboratory designed to throw light upon the probability of a quinoid formula for the red hydrochlorides.

An explanation, differing from any of the above, has occurred to us since reading a recent article by Anselmino[1] which came to our notice after the experimental work described in this paper was practically completed. Anselmino found that when *p*-homosalicylic aldehyde is condensed with aniline the product formed exists in two different forms, a red and a yellow. That this is not simply a case of dimorphism is shown by the fact that the two forms differ in chemical behavior and give different derivatives. The most probable assumption concerning their constitution would seem to be that they are stereoisomeric in the same sense as the isomeric oximes of unsymmetrical ketones. If we try to explain the behavior of the compounds we are studying upon a similar basis, we should have to say that the salts vary in color because they are derived from different stereoisomeric bases, one red, the other yellow; that in the case of the bases themselves, the yellow form is alone stable; that when the bases add hydrochloric acid, the yellow salts first formed are unstable and go over to form salts of the other — red base; finally, when the saturated salts are formed, that a transformation in the opposite sense takes place. This explanation disregards the question as to which nitrogen holds the hydrochloric acid. Now, in this connection, we have to remember that previous to this recent work of Anselmino, no well-attested cases of stereoisomerism had been observed among benzylidene compounds, though they have long been looked for; and, further, that Anselmino himself observed no such isomerism in the case of the salts. In fact he points out that his red and yellow bases gave identical hydrochlorides. This, of course, is no conclusive argument against a stereochemical explanation of the facts which we have observed. It does, however, furnish a reason for not accepting such an explanation hastily.

It will be seen in the experimental part of this paper that the salts of salicylidene *p*-aminodimethylaniline undergo change in color on standing, and it has been already pointed out that compounds of this class containing the diethylamino group show similar behavior. From what has already been said, it will be seen in what a variety of directions an explanation of this fact might be sought. Any discussion of these

[1] Ber., 40, 3465 (1907); also *Ibid.*, 38, 3989 (1905).

possibilities would, however, be premature until more work upon these ethyl compounds has been done. For the present also we wish to reserve any opinion as to the probable formulæ of the red hydrochlorides.

Experimental Part

The condensation product of *p*-aminodimethylaniline with benzaldehyde was first prepared by Calm.[1] It is interesting to note his observation that this base adds two molecules of hydrochloric acid to form a "white" salt. This illustrates the light color of the saturated hydrochloride, and at the same time shows that Calm attached no significance to the formation of the red intermediate product. He gives a determination of chlorine in the saturated salt. The other bases studied in this paper were prepared by Nuth[2] at the suggestion of Calm. He did not prepare salts. We have little to add to his description of the bases, except for some melting points already corrected by more recent observers. We prepared the bases by mixing molecular quantities of the amine with the various aldehydes, sometimes warming a little on the water bath. The reaction then proceeded at once and gave good yields. The product was recrystallized once from alcohol. It was usually found that further recrystallization did not raise the melting point. The bases range in color from a light yellow to a light orange.

In studying the salts we at first allowed hydrochloric acid to act upon the bases in the dry state. When piperonylidene *p*-aminodimethylaniline, for example, is spread upon a piece of porcelain (a crucible cover) and a current of hydrochloric acid passed over it, the mass suddenly turns a deep red. This color no sooner appears than it begins again to fade, owing to the formation of the light yellow saturated salt. A similar effect is produced when the base is dissolved in dry ether and hydrochloric acid gas introduced. Here the liquid first turns dark red; then a precipitate of the same color appears, and finally, the time varying with the amount of substance present, the color of the solution grows rapidly lighter in shade, the precipitate becomes bright yellow, and at the end the supernatant liquid is colorless, the saturated salt being practically insoluble in ether. It will frequently be noticed that at the mouth of the tube where the gas enters, and where consequently the acid is always in excess, a yellow deposit of the dihydrochloride

[1] Ber., 17, 2938 (1884).

[2] *Ibid.*, 18, 573 (1885).

forms at once. This makes it probable that the red salt, however it is prepared, contains a good deal of the yellow enclosed. This shows itself in the analytical data furnished further on. When the salts were prepared for analysis, the following procedure was employed in order to avoid this kind of contamination as much as possible. First, the free base was dissolved in sodium-dried ether, and then a solution of hydrochloric acid in dry ether was run in from a burette. When preparing the saturated salt, the addition of the acid solution was continued as long as any precipitate formed. To prepare an unsaturated salt, a little less than half as much acid was added as had been found necessary in preparing the saturated one. The precipitates so obtained were filtered by suction, washed repeatedly with dry ether, and finally dried in a vacuum desiccator containing both concentrated sulphuric acid and sticks of caustic soda. If lumps formed during the drying, these were ground up and the desiccation continued. As far as our observation goes, these salts melt only with decomposition, and the temperature observed depends largely upon the time of heating. In the case of the saturated salts, the point of decomposition lies quite close to 200° in almost all cases. The chlorine determinations were in all cases made by the Carius method. The salts precipitated and dried as above described were used for analysis without recrystallization. Alcohols would have been the only practicable solvents for this purpose, but some experiments made in this direction led us to fear the contaminating effects of hydrolytic action. As we have pointed out above, the salts were probably more or less contaminated with each other, and perhaps also with the free bases. Under the circumstances we have not thought it desirable to make a large number of determinations, in the hope that some of them might agree more closely with the results of theoretical computation. In spite of the wide divergence to be observed in many cases, we think that the numerical results make plain the one point which we wish to emphasize at this time, namely, that the light-colored salts contain about one molecule of acid more than the dark ones. The results follow:

Benzylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{15}H_{16}N_2.HCl$, Cl, 13.60; found, 17.01. Saturated hydrochloride: calculated for $C_{15}H_{16}N_2.2HCl$, Cl, 23.09; found, 20.48.

Cinnamylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{17}H_{18}N_2.HCl$, Cl, 12.36; found, 15.33. Saturated hydrochloride: calculated for $C_{17}H_{18}N_2.2HCl$, Cl, 21.95; found, 21.34.

Piperonylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{16}H_{16}O_2N_2.HCl$, Cl, 11.63; found, 15.19. Saturated hydrochloride: calculated for $C_{16}H_{16}O_2N_2.2HCl$, Cl, 20.78; found, 21.12, 21.05.

Salicylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{15}H_{16}ON_2.HCl$, Cl, 12.81; found, 13.07. Saturated hydrochloride: calculated for $C_{15}H_{16}ON_2.2HCl$, Cl, 22.65; found, 22.47.

The color of the salts seemed less permanent in this case than in any we had previously studied. Nuth records that the free base turns red on standing in the air, and we notice that the red hydrochloride has a tendency to grow lighter in color. What is perhaps more curious is that the saturated hydrochloride, which when first precipitated is almost colorless, grows considerably darker in color. We have since met with even more marked changes of this kind in the study of the bases formed by condensing *p*-aminodiethylaniline with aldehydes. We consider any theoretical discussion of this phenomenon to be premature until these diethyl compounds have been more thoroughly studied. The fact should be borne in mind, however, that, according to Anselmino, salicylic aldehyde is one of those which forms isomeric aniles, one red, the other yellow.

Anisylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{16}H_{18}ON_2.HCl$, Cl, 12.20; found, 12.20. $C_{16}H_{18}ON_2.2HCl$, Cl, 21.68; found, 18.34. Saturated hydrochloride: calculated for $C_{16}H_{18}ON_2.3HCl$, Cl, 29.27; found, 28.78, 26.16, 26.61.

In view of the fact that in the case of the red hydrochlorides high results for chlorine are usually obtained, probably owing to the tendency of these salts to enclose some of the saturated compounds, the numerical results given above leave it a little in doubt whether the red salt in this case contains, when pure, one or two molecules of acid. It is quite evident, however, that the saturated salt contains nearly three molecules. This seems to be one of those cases referred to by Baeyer[1] where a base shows itself capable of combining with more acid than its formula accounts for. It might be supposed that in both salts the additional molecule of hydrochloric acid attached itself to the methoxyl group to form an oxonium salt. This may be the correct explanation, but it is not necessarily so; for we find that the most simply constituted member of the whole group, benzylidene aniline, though it contains but one

[1] Ber., 38, 1157 (1905).

nitrogen and no oxygen, yet adds two molecules of hydrochloric acid, as shown by the following analysis:

Calculated for $C_{13}H_{11}N.HCl$, Cl, 16.29; for $C_{13}H_{11}N.2HCl$, Cl, 27.90; found, 27.68, 27.62.

We were much surprised at this result, as it raised the question whether all of the benzylidene compounds containing one nitrogen might not behave similarly, and whether in those containing two atoms all of the acid might not be held by one nitrogen. The analyses of the salts of the three following compounds, however, show that the addition of more molecules of acid than there are nitrogen atoms in the base is the exception; though from what has gone before, it may well be of more frequent occurrence than has hitherto been supposed.

Piperonylidene Aniline. — This base was first prepared by Lorenz.[1] It is absolutely colorless, the first of these compounds which we have been able to prepare in that condition. The hydrochloride is bright yellow, and this makes perhaps the most striking example of simple "halochromy" which we have observed in the group. The hydrochloride contains but one molecule of acid, as is shown by the following analytical data:

Calculated for $C_{14}H_{11}O_2N.HCl$, Cl, 13.55; found, 13.76, 13.51.

Piperonylidene p-Toluidine. — This substance crystallizes from alcohol in cream-colored prisms which melt at 98°.

Calculated for $C_{15}H_{13}O_2N$, C, 75.26; H, 5.48; N, 5.87; found, 75.28, 5.55, 6.11.

The hydrochloride is light yellow. The percentage of chlorine was determined. Calculated for $C_{15}H_{13}O_2NHCl$, Cl, 12.86; found, 13.03, 12.98.

Piperonylidene p-Chloraniline. — The base melts at 78°. It has not been analyzed. It forms a light yellow hydrochloride. Calculated for $C_{14}H_{10}O_2NCl.HCl$, Cl, 23.95; found, 23.43.

We wished to learn something of the color of salts analogous to those formed by condensing aldehydes with *p*-aminodimethylaniline, but which contained an amino group not substituted by alkyl radicals. We had some hopes that at least a small yield of such compounds might be obtained by condensing one molecule of aldehyde with one of a diamine. Accordingly we treated piperonal with *p*-phenylenediamine, and also with benzidine. In both cases the only products we obtained were those

[1] Ber., 14, 792 (1881).

formed by the condensation of one molecule of diamine with two molecules of piperonal. These bases are soluble with difficulty in alcohol, ether, or the aromatic hydrocarbons. They can be crystallized from nitrobenzene, from which they separate in bronze yellow scales of a semi-metallic luster. The compound with *p*-phenylenediamine melts at 216°. Calculated for $C_{22}H_{16}O_4N_2$, C, 70.94; H, 4.33; N, 7.55; found, 70.30, 4.52, 7.90.

The compound formed by condensing benzidine with piperonal melts not quite sharply at 241°. The liquid formed is not transparent, and it is possible that it is crystalline in character, as liquid crystals are not infrequently met with among compounds of similar constitution. The composition of the base was verified by a nitrogen determination. Calculated for $C_{28}H_{20}O_4N_2$, N, 6.50; found, 6.43.

We add some incomplete data concerning some substances prepared during the present investigation, but which, as they have no further theoretical interest for us, will probably not be worked with further.

Piperonylidine p-Aminoethylbenzoate. — This substance was prepared by condensing piperonal with *p*-aminoethylbenzoate. The base melts at 109°, is almost colorless, and forms a yellow hydrochloride.

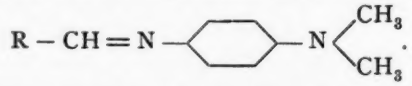
Calculated for $C_{17}H_{15}O_4N$, C, 68.64; H, 5.09; N, 4.72; found, 68.34, 5.08, 4.84.

Piperonal condenses readily with *m*-nitraniline to form a base which melts at 119°. This forms a yellow hydrochloride. We have a nitrogen determination in the free base. Calculated for $C_{14}H_{11}O_4N_2$, N, 10.35; found, 10.56.

Piperonal condenses with *p*-bromaniline to form a product melting at 109°. This forms a hydrochloride of a light canary-yellow color. We have analyzed neither the base nor the salt.

Summary

When *p*-aminodimethylaniline is treated with aromatic aldehydes, condensation products are formed which have the general formula,



These bases add one molecule of hydrochloric acid to form dark red salts of a much deeper color than the free bases. The addition of more hydrochloric acid produces salts of a light yellow color, lighter than that of the free base.

Three explanations of this behavior are considered:

(1) That the first molecule of acid adds to the auxochrome nitrogen augmenting the color, while the second adds to the chromophore nitrogen, changing its valence and consequently destroying its chromophore character.

(2) That the monohydrochloride has a quinoid structure, while the saturated salt and the free base are benzoid.

(3) That there is a double series of stereoisomeric red and yellow bases and salts, the red form of the monohydrochloride being the stable one, the yellow form being stable in the other cases.

A decision as to which of these explanations is most applicable must be deferred until more experimental material can be collected.

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A REVISION OF THE FUNDAMENTAL LAWS OF MATTER AND ENERGY

BY GILBERT N. LEWIS

RECENT publications of Einstein[1] and Comstock[2] on the relation of mass to energy have emboldened me to publish certain views which I have entertained on this subject and which a few years ago appeared purely speculative, but which have been so far corroborated by recent advances in experimental and theoretical physics that it seems desirable to subject these views to a strict logical development, although in so doing it will be necessary to modify those fundamental principles of the mechanics of ponderable matter which have remained unaltered since the time of Newton.

The recent experiments which indicate a change in the mass of an electron with the speed, together with the phenomenon of radio-activity, have in some minds created a doubt as to the exact validity of some of the most general laws of nature. In the following pages I shall attempt to show that we may construct a simple system of mechanics which is consistent with all known experimental facts and which rests upon the assumption of the truth of the three great conservation laws, namely, the law of conservation of energy, the law of conservation of mass, and the law of conservation of momentum. To these we may add, if we will, the law of conservation of electricity.

THE RELATION OF MASS TO ENERGY

When a black body[3] is placed in a beam of light it is subject to a pressure or force which tends to move it in the direction in which the light is moving. If $\frac{dE}{dt}$ denotes the time rate at which the body

[1] Ann. Phys., 18, 639 (1905).

[2] Phil. Mag., 15, 1 (1908).

[3] In place of a black body we might consider a partially reflecting one. The equations thus obtained are more complicated, but lead also to the simple equation (7).

receives energy, f the force, and V the velocity of light, we have in rational units the formula,

$$f = \frac{1}{V}\frac{dE}{dt} \tag{1}$$

This important equation, which was obtained by Maxwell as a consequence of his electromagnetic theory, and by Boltzmann through the direct application of the laws of thermodynamics, has recently been verified with remarkable precision in the beautiful experiments of Nichols and Hull.[1]

A body subjected to the pressure of radiation will acquire momentum, and if we are to accept the law of conservation of momentum we must conclude that some other system is losing in the same direction an equivalent momentum. We are thus led inevitably, as Poynting has shown, to the idea that the beam of radiation carries not only energy, but momentum as well.

The body subject to the constant force of radiation f will obviously acquire momentum at the rate,

$$\frac{dM}{dt} = f. \tag{2}$$

Combining equations (1) and (2) gives,

$$\frac{dE}{dM} = V. \tag{3}$$

The ratio of the acquired energy to the acquired momentum is equal to the velocity of light. The beam of radiation must, therefore, possess energy and momentum in the same ratio. Hence for the beam itself, or any part of it,

$$\frac{E}{M} = V. \tag{4}$$

To any one unfamiliar with the prevailing theories of light, knowing only that light moves with a certain velocity and that in a beam of light momentum and energy are being carried with this same velocity, the natural assumption would be that in such a beam *something possessing mass moves with the velocity of light and therefore has momentum and energy*. Notwithstanding its apparent divergence from the commonly accepted light theories, I propose to adopt this view and see whither it leads.

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[1] Phys. Rev., 17, 26 and 91 (1903).

Postulating the validity of the fundamental conservation laws mentioned above, we shall need in the following development only this one cardinal assumption, that a beam of radiation possesses not only momentum and energy, but also mass, traveling with the velocity of light, and that a body absorbing radiation is acquiring this mass as it also acquires the momentum and the energy of the radiation. Therefore a body which absorbs radiant energy increases in mass.

The amount of this increase is readily found. If in general we write momentum as the product of mass and velocity, then the momentum of any part of a beam of radiation having the mass m will be given by the equation,

$$M = mV. \tag{5}$$

The increase dM in the momentum of the body absorbing the radiation will therefore equal the increase dm in its mass, multiplied by the velocity of light.

$$dM = Vdm. \tag{6}$$

Combining this equation with (3), we find

$$dm = \frac{dE}{V^2}, \tag{7}$$

or if we write $V = 3 \times 10^{10}$ cm. per second,

$$dm = 1.111 \times 10^{-21}\, dE.$$

Thus a body receiving or emitting radiant energy gains or loses mass in proportion, and by the amount 1.111×10^{-21} grams for every erg. This is a small quantity indeed, but one which is not to be neglected.

Assuming the fundamental conservation law, we must regard mass as a real property of a body which depends upon its state and not upon its history. Hence it is obvious that if in any other way than by radiation the body gains or loses energy, it must still gain or lose mass in just the above proportion. In other words, any change in a body's content of energy is accompanied by a definite change in its mass, regardless of the nature of the process which the energy change accompanies.[1]

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[1] I was first led to an investigation of the relation of mass to energy by the work of Landolt on the change of weight in chemical reactions. But it is obvious from equation (7) that although there always will be a loss of mass in a reaction which is accompanied by the evolution of energy, this loss in the case of any ordinary reaction will be far too small to measure. In fact, Landolt has very recently shown (Ber. Berlin. Akad., 1908, 354) that when all possible precautions are taken there is no measurable change of weight in the reactions which he studied.

Since, therefore, when a body loses a given quantity of energy it always loses a definite quantity of mass, we might assume that if it should lose all its energy it would lose all its mass, or, in other words, that the mass of a body is a direct measure of its total energy, according to the equation,

$$m = \frac{E}{V^2} \tag{8}$$

We should then regard mass and energy as different names and different measures of the same quantity, and say that 1 gram equals 9×10^{20} ergs in the same sense that we say that one meter equals 39.37 . . . . inches.

Plausible as this view seems, it rests upon an additional hypothesis besides the fundamental postulate which we have chosen. We shall use, therefore, not equation (8) but equation (7) as the basis of the following work.

It is to be noted that equation (8) has also been obtained by Einstein (*loc. cit.*), who derived it from the general equations of the electromagnetic theory, with the aid of the so-called principle of relativity. That a different method of investigation thus leads to the same simple equation we have here deduced speaks decidedly for the truth of our fundamental postulate.[1]

Comstock (*loc. cit.*), from electromagnetic theory alone, has also concluded that mass is proportional to energy, but his equation is

$$m = \frac{4}{3}\,\frac{E}{V^2}.$$

To investigate, for the cases studied by Comstock, the cause or the justification for this appearance in the equation of the factor $\frac{4}{3}$ would lead too far into electromagnetic theory, from which in the present paper I wish to hold entirely aloof.

Before proceeding to develop fully the consequences of equation (7) it may be well to point out an apparent inconsistency in the equations for the momentum and the energy of a beam of radiation. The momentum of the beam of mass m we have given in equation (5) as

$$M = mV.$$

From our assumption that the energy of the beam is simply the kinetic

[1] Einstein, however, obtains (8) as an approximate formula, while we obtain both (7) and (8) as perfectly exact equations.

energy of the moving mass m, we might expect from our knowledge of elementary mechanics to find for the energy the equation,

$$E = \tfrac{1}{2} m V^2,$$

whereas, in fact, we find from equations (4) and (5) that

$$E = m V^2. \tag{9}$$

We shall see, however, in the next section that this comparison of equations (5) and (9), instead of demolishing our theory, actually furnishes a remarkably satisfactory argument in its favor.

Non-Newtonian Mechanics

One of the interesting branches of modern mathematics has grown out of the study of those geometries which would result from the change of one or more of the axioms of Euclid. These non-Euclidian geometries present the properties of purely imaginary kinds of space, and are therefore so far mere exercises in logic, without any physical significance. But their investigation was doubtless prompted in some cases by the belief that experiment itself may sometimes show that there are deviations from the ordinary laws of space when these laws are subjected to tests of a different order from those of common mensuration. Indeed it is not unlikely that Euclidian geometry may prove inadequate when we are able to subject to an accurate metric investigation the vast stretches of interstellar space or the minute regions which we believe to be encompassed within an atom or an electron.

The science of mechanics, like geometry, has been built up from a set of simple axioms, which were laid down by Newton. But the conclusions of the previous section lead us to modify one of these axioms and thus lay the foundation of a system of non-Newtonian mechanics.

The axiom which we must surrender is the one which states that the mass of a body is independent of its velocity. We have concluded that mass is proportional to content of energy. When a body is set in motion it gains kinetic energy, and therefore its mass must change with its velocity. In place of the axiom which we have abandoned we must substitute equation (7).

Before investigating the consequences of this step it is necessary to define exactly the principal mechanical quantities which we are to use.

Extension in space (l) and time (t) will be measured in the usual way and the centimeter and the second will be employed as units.

Force (f) will be given its usual significance, and the unit, the dyne, will be that force which, acting upon the international standard kilogram when the latter is at rest, imparts to it an initial acceleration of .001 $\frac{\text{cm}}{\text{sec}^2}$.

The momentum (M) of a moving body will be measured by the time in which it is brought to rest under the influence of a constant opposing force of one dyne acting in the line of its motion.

The mass (m) of a moving body will be defined as the momentum divided by the velocity (v), that is,

$$m = \frac{M}{v}. \tag{10}$$

The limiting ratio of the momentum of a body to its velocity, when it is brought to rest, will be called its mass when at rest. The unit of mass is the gram.

The kinetic energy (E') of a body will be measured by the distance through which it will move before being brought to rest by a constant opposing force of one dyne acting in the line of the body's motion. The unit of energy will be the erg.

These definitions, although somewhat unusual in form, are perfectly consistent with the ordinary definitions of Newtonian mechanics. But they have been so chosen as to be consistent also with equation (7) and the fundamental conservation laws. Obviously equation (7) itself is not inconsistent with these conservation laws, for although a body increases in mass as it gains kinetic energy, some other system is losing the same mass as it loses the same energy.

In accordance with the above definitions we may write,

$$dM = fdt. \tag{11}$$

$$dE' = fdl. \tag{12}$$

Let us consider a body, originally moving with a velocity v, subjected for the time dt to a force f in the line of its motion. Its momentum and kinetic energy will change according to (11) and (12) by the amounts,

$$dM = fdt,$$

$$dE' = fdl = fvdt.$$

Hence

$$dE' = vdM. \tag{13}$$

So far the equations are those of Newtonian mechanics, but now in substituting for M from equation (10) we must regard m as a variable, and write,

$$dE' = mvdv + v^2dm. \tag{14}$$

This will be our fundamental equation connecting the kinetic energy of a body with its mass and velocity.

Introducing now the relation of mass to energy given in equation (7), we may write,

$$dE' = V^2dm,$$

and combining this equation with (14) gives,

$$V^2dm = mvdv + v^2dm.$$

This equation, containing only two variables, m and v, and the constant V, may readily be integrated as follows: By a simple transformation,

$$\left(1 - \frac{v^2}{V^2}\right)dm = \frac{mvdv}{V^2}.$$

Writing $\beta = \frac{v}{V}$, and noting that

$$\frac{vdv}{V^2} = -\tfrac{1}{2}\,d(1 - \beta^2),$$

we see that

$$\frac{dm}{m} = -\tfrac{1}{2}\,\frac{d(1 - \beta^2)}{1 - \beta^2}.$$

Hence

$$\log m = -\tfrac{1}{2}\log(1 - \beta^2) + \log m_o,$$

where $\log m_o$ is the integration constant. Therefore,

$$\log \frac{m}{m_o} = \log (1 - \beta^2)^{-\frac{1}{2}}, \quad \text{or,}$$

$$\frac{m}{m_o} = \frac{1}{(1 - \beta^2)^{\frac{1}{2}}}. \tag{15}$$

This is the general expression for the mass of a moving body in terms of β, the ratio of its velocity to the velocity of light. When β is zero, $m = m_o$. m_o represents, therefore, the mass of the body at rest.

If we substitute in this equation numerical values of β we find that, while the quotient $\frac{m}{m_o}$ becomes infinite when the velocity equals the velocity of light, it remains almost equal to unity until the velocity of

light is closely approached. Thus a ton weight given the velocity of the fastest cannon ball would, according to this equation, gain in mass by less than one-millionth of a gram. It is obvious that, except in those unusual cases in which we deal with velocities comparable with that of light, our non-Newtonian equations are identical with those of ordinary mechanics far within the limits of error of the most delicate experiments.

Recently, however, it has been possible to study, in the negative particles emitted by radio-active substances, bodies which sometimes move with a velocity only a little less than that of light. In a series of remarkably skillful experiments Kaufmann [1] was able to measure the ratio of electric charge to mass $\left(\frac{e}{m}\right)$ for negative particles moving at different speeds. Assuming that the charge is constant, the fact that $\frac{e}{m}$ varies with the speed of the particle must be attributed to a variation of the mass with the speed. On this assumption it is possible to calculate from Kaufmann's experiments the values of $\frac{m}{m_o}$ at the different velocities.

The mass of a negative particle is usually spoken of as electromagnetic mass, but if we are to hold to our definitions we must recognize only one kind of mass. In general, we have defined the mass of a moving body as the quotient of the time during which it will be brought to rest by unit force, divided by the initial velocity. It matters not what the supposed origin of this mass may be. Equation 15 should, therefore, be directly applicable to the experiments of Kaufmann. In the following table are given the values of $\frac{m}{m_o}$ found for the different observed values of β in the second column. The third column shows those values of β which would correspond with the same values of $\frac{m}{m_o}$ according to equation (15).

[1] Phys. Zeit., 4, 54 (1902); Ann. Phys., 19, 487 (1906).

$\frac{m}{m_0}$	β (observed).	β (calculated).
1.0	0.0	0.0
1.34	0.73	0.67
1.37	0.75	0.69
1.42	0.78	0.71
1.47	0.80	0.73
1.54	0.83	0.76
1.65	0.86	0.80
1.73	0.88	0.82
2.05	0.93	0.88
2.14	0.95	0.89
2.42	0.96	0.91

It will be seen that the observed values of β follow to a remarkable degree the same trend as those which are calculated by equation (15), but are in every case 6 to 8 per cent. higher.[1] I believe that these differences lie within the limits of experimental error of Kaufmann's measurements. It is true that he claims a higher degree of accuracy, but, notwithstanding the extreme care and delicacy with which the observations were made, it seems almost incredible that measurements of this character, which consisted in the determination of the minute displacement of a somewhat hazy spot on a photographic plate, could have been determined with the precision claimed. Moreover, Planck[2] and Stark[3] have pointed out certain corrections which probably should have been made by Kaufmann and which would produce a material change in his results.[4]

That a charged particle must possess mass in virtue of its charge, and that this mass must vary with the velocity of the particle, was shown to be a consequence of the electromagnetic theory by J. J.

[1] The constancy of the difference between the observed and calculated values of β is striking and would alone indicate some constant error in Kaufmann's results.

[2] Verhandlung Deutsch. Phys. Ges., 9, 301 (1907).

[3] *Ibid.*, 10, 14 (1908).

[4] In reply to Planck, see Kaufmann, *Ibid.*, 9, 667 (1907).

Thomson and by Heaviside, and numerous attempts have been made to find the exact expression for the change of mass with the velocity. But before this can be done some assumption is necessary as to the shape of the particle and the distribution of its charge. The three theories of the simple negative particle or electron which are now most discussed are due to Abraham, Bucherer, and Lorentz.[1] The first assumes that the electron is and remains a rigid sphere; the second assumes an electron which is spherical when at rest, but which in motion contracts in the direction of its translation and expands laterally so as to keep a constant volume; the third assumes an electron similar to the second, which contracts in the direction of translation, but which does not change its other dimensions. On the basis of these theories and from known electromagnetic principles three equations have been obtained for the value of $\frac{m}{m_o}$ as a function of β, namely

$$(a) \quad \frac{m}{m_o} = \tfrac{3}{4} \frac{1}{\beta^2}\left(\frac{1+\beta^2}{2\beta} \log \frac{1+\beta}{1-\beta} - 1\right).$$

$$(b) \quad \frac{m}{m_o} = \frac{1}{(1-\beta^2)^{\frac{1}{2}}}.$$

$$(c) \quad \frac{m}{m_o} = \frac{1}{(1-\beta^2)^{\frac{1}{2}}}.$$

The extraordinary significance of the similarity of the first two of these equations and the identity of the third with equation (15), which we have derived from strikingly different principles, needs no emphasis. Kaufmann shows that his results agree better with the first two of these equations than with the third; but to regard this as serious evidence as to the validity of equation (15) would, as Planck has pointed out, be laying too great a stress on the accuracy of the experimental observations.

The agreement of Kaufmann's results with the above equations has led him, and all others who have discussed his results, to the conclusion that all of the mass of an electron is electromagnetic.

Their argument is based on the assumption that ordinary mass — the mass of "ponderable matter" — is independent of the velocity, while "electromagnetic mass" varies with the velocity according to one of

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[1] For a discussion of these theories, see Abraham, Theorie der Elektricität, 2, Leipzig, 1905; and Bucherer, Mathematische Einführung in die Elektrontheorie, Leipzig, 1904.

the above equations. But in this paper we have assumed that all mass is one, and that any bodies, whether charged or not, moving at the velocities of Kaufmann's electrons would show the same values of $\frac{m}{m_o}$.

There is some hope that the correctness of this view may be decided by an experimental study of the mass of a positive or α particle at different speeds. According to the ordinary view the mass of such a positive particle as issues from a radio-active source is chiefly that of its "ponderable" matter and only to a very small extent "electromagnetic mass." It would, therefore, be generally assumed that at the highest velocity of the particle, about one-tenth of the velocity of light, it would have substantially the same mass as at rest. According to our view, on the other hand, the mass of this or any other particle would change with the velocity in the same way as the mass of an electron. From equation (15) we should, therefore, expect the particle moving with one-tenth of the velocity of light to have a mass 2 per cent. greater than when at rest. The experimental difficulties in testing this point would be very great, of course, but perhaps not insurmountable.

The plausibility of our fundamental assumption which led directly to equation (15) has been greatly increased by the agreement between this equation and Kaufmann's results, and also perhaps by the similarity between this equation and those deduced from electromagnetic theory. But the simplest as well as the strongest evidence of the correctness of our point of view comes from a consideration of the non-Newtonian equation for kinetic energy.

The integration of equation (14) obviously does not yield the simple Newtonian equation,

$$E' = \tfrac{1}{2}\, mv^2.$$

This equation must be replaced by one that is obtained as follows:

Let a body, which at rest has the mass m_o, be given the velocity v. As its energy changes, its mass will change according to equation (7), and

$$m - m_o = \frac{E'}{V^2};$$

where E' is the acquired kinetic energy and $m - m_o$ is the increase in mass. Eliminating m_o between this equation and (15) gives

$$E' = m V^2 [1 - (1 - \beta^2)^{\frac{1}{2}}]. \qquad (16)$$

This is the general formula for the kinetic energy of a moving body.

As usual, β represents $\frac{v}{V}$, the ratio of the velocity to the velocity of light.

From equations (10), (15), and (16) may be constructed the whole science of non-Newtonian dynamics, of which Newtonian dynamics furnishes a limiting case, namely, for velocities which are negligible in comparison with the velocity of light.

For example, expanding (16) by the binomial theorem gives

$$E' = m V^2(\tfrac{1}{2}\beta^2 + \tfrac{1}{8}\beta^4 \ldots). \tag{17}$$

For low values of β the higher terms may be neglected and

$$E' = \tfrac{1}{2} mv^2.$$

That is, the limit approached by the kinetic energy of a body as the velocity approaches zero is, as in ordinary mechanics, one-half the product of the mass and the square of the velocity. At the other limit of velocity when $\beta = 1$ it follows from (16) that

$$E' = m V^2. \tag{18}$$

Between these two limits it is obvious that

$$\tfrac{1}{2} mv^2 < E' < mv^2.$$

The momentum and the kinetic energy of any mass moving with the velocity of light are, therefore,

$$M = m V,$$
$$E' = m V^2;$$

but these equations are identical with (5) and (9), which we obtained for the momentum and the energy of a *beam of light.*

Further Consequences of the Theory

The view here proposed, which appears at first sight a reversion to the old corpuscular theory of light, must seem to many incompatible with the electromagnetic theory. If it were really so I should not have ventured to advance it, for the ideas announced by Maxwell constitute what may no longer be regarded as a theory, but rather a body of experimental fact. The new theory is offered, not in any sense to replace, but to supplement the accepted theories of light. I hope in another paper to show that it is entirely consistent with those theories.

Such a proof may constitute a step towards one of the obvious goals of present day science, the complete mechanical explanation of electromagnetic phenomena, or, what is very nearly the same thing, an electromagnetic explanation of the phenomena of ordinary mechanics. In the meantime a few of the more salient conclusions of our theory may be cursorily examined.

In the first place, it should be noticed that, while the theory is consistent with a modified corpuscular theory of light, it does not necessarily imply that light is corpuscular. The stream of mass issuing from a radiating body may be made up of discrete particles or it may be continuous. In the absence of any evidence on this point we may assume the latter. Whatever it may be that is emitted, it is not matter in the ordinary sense, as is to be seen from the following considerations.

According to equation (15), any body of finite mass increases in mass as it increases in velocity, and would possess infinite mass if it could be given the velocity of light. *Therefore that which in a beam of light has mass, momentum, and energy, and is traveling with the velocity of light, would have no energy, momentum, or mass if it were at rest, or, indeed, if it were moving with a velocity even by the smallest fraction less than that of light.* After this extraordinary conclusion it would at present be idle to discuss whether the same substance or thing which carries the radiation from the emitting body continues to carry it through space, or, indeed, whether there is any substance or thing connected with the process.

If we assume an ether pervading space and assume that this ether possesses no mass except when it moves with the velocity of light, it is obvious that an ether drift could in no way affect a beam of radiation nor be detected by any mechanical means. If we are to assume such an ether we may as well assume it to be at rest.

The question whether a method is conceivable by which absolute motion in space may be distinguished from relative motion must be answered definitely in the affirmative by one who accepts the above equations of non-Newtonian mechanics. A body is absolutely at rest when any motion imparted to it increases its mass, or when a certain force will give it the same acceleration in any direction. It is true that metaphysicians hold that in the strictest sense absolute motion is not only unknowable, but unthinkable; but we may say at least that the above method permits theoretically the detection of absolute trans-

lational motion in the same sense that a study of centrifugal forces enables us to detect absolute rotational motion.

Summary

It is postulated that the energy and momentum of a beam of radiation are due to a *mass* moving with the velocity of light.

From this postulate alone it is shown that the mass of a body depends upon its energy content. It is therefore necessary to replace that axiom of Newtonian mechanics according to which the mass of a body is independent of its velocity, by one which makes the mass increase with the kinetic energy.

Retaining all the other axioms of Newtonian mechanics and assuming the conservation laws of mass, energy, and momentum, a new system of mechanics is constructed.

In this system momentum is mv, kinetic energy varies between $\frac{1}{2}mv^2$ at low velocity and mv^2 at the velocity of light, while the mass of a body is a function of the velocity and becomes infinite at the velocity of light. The equation obtained agrees with the experiments of Kaufmann on the relation between the mass of an electron and its velocity. It is, moreover, strikingly similar to the equations that have been obtained for electromagnetic mass.

The new view leads to an unusual conception of the nature of light. It offers theoretically a method of distinguishing between absolute and relative motion.

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
May 14, 1908.

PROCEEDINGS OF THE SOCIETY OF ARTS

FORTY-SIXTH YEAR, 1907-1908

BOSTON, February 13, 1908.

THE 645th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, February 13, at eight o'clock, about one hundred and sixty persons being present. Dr. Robert P. Bigelow presided.

Mr. F. W. McCarter was elected to membership.

The chairman introduced Professor Thomas A. Jaggar, Jr., of the Institute of Technology, who spoke on "The Evolution of Bogoslof, a New Volcano in Behring Sea." Professor Jaggar's address was illustrated by a large number of lantern slides, many of which were taken by his party during a recent excursion to the Behring Sea. He gave a most interesting account of the volcanic origin of this island in the Behring Sea, and his slides clearly showed the island of Bogoslof in its several different conditions since it first rose from the sea. The thanks of the Society were extended to the speaker by the chairman, and the meeting adjourned at 9.30.

BOSTON, February 27, 1908.

The 646th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, February 27, at eight o'clock, about one hundred and thirty persons being present. Colonel Edmund H. Hewins presided.

The chairman introduced Mr. Charles B. Burleigh, of the General Electric Company, Boston, who discussed in a most interesting manner the essential features of steam turbines generally, and of the Curtis turbine in particular. Mr. Burleigh held the attention of the audience until 9.30, showing nearly one hundred lantern slides. After the address

an interesting discussion followed, and many questions were asked. The chairman extended the thanks of the Society to the speaker. The meeting adjourned at 10.15.

BOSTON, March 12, 1908.

The 647th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 12, at eight o'clock, about one hundred persons being present. Dr. Robert P. Bigelow presided.

The chairman introduced Mr. Gorham Dana, Manager of the Underwriters' Bureau of New England, who gave a most interesting talk on "Recent Developments in Fire Protection Devices."[1] The lecture was illustrated by a large number of specimens and some excellent lantern slides. The chairman extended the thanks of the Society to the speaker, and the meeting adjourned at 9.45.

BOSTON, March 26, 1908.

The 648th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 26, at eight o'clock, about two hundred and thirty persons being present. Professor Charles R. Cross presided.

The chairman then introduced Mr. J. E. Brulatour, of the Lumière Company, who spoke on "The Lumière Autochrome Plates." Mr. Brulatour showed numerous slides made on these plates and explained the process of the three-color photography. He had but little to say, allowing the slides to speak for themselves. A large number of most interesting slides were shown and many questions were asked of Mr. Brulatour at the close of the address. He also showed a large number of color plates, too large for insertion in the lantern. The thanks of the Society were extended to the speaker by the chairman, and the meeting adjourned at 9.30.

BOSTON, April 9, 1908.

The 649th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, April 9, at eight

[1] Printed above, pp. 141–163.

o'clock, about sixty persons being present. Professor R. H. Richards presided.

The chairman introduced Mr. E. G. Acheson, President of the Acheson International Graphite Company, of Niagara Falls, who spoke on "The Deflocculation of Nonmetallic Amorphous Bodies, with Special Reference to Graphite as a Lubricant." Mr. Acheson's talk was illustrated by numerous experiments, clearly showing the means by which his deflocculated, or finely divided, graphite could be permanently suspended in water by the addition of a small amount of vegetable matter, and how readily acids or other impurities caused its precipitation. As a lubricant it can be suspended in either water or oil, and has produced remarkable results both as a cylinder oil and as an ordinary spindle lubricant. It has even been suggested that lubricating projectiles used in our large guns will greatly prolong the life of the rifle, which ordinarily is good for less than one hundred shots. The intense friction of the projectile at the high velocities attained quickly destroys the gun. The graphite would largely reduce this friction and increase the muzzle velocity. The Society extended a vote of thanks to the speaker, and the meeting adjourned at 9.30.

BOSTON, April 23, 1908.

The 650th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, April 23, at eight o'clock. Colonel Edmund H. Hewins presided.

The chairman introduced Professor Dugald C. Jackson, Head of the Department of Electrical Engineering, Institute of Technology, who spoke on "Factors Governing the Rates of Public Service Corporations and the Government Control of Rates." The lecture was of timely interest and will appear in the next issue of the TECHNOLOGY QUARTERLY. The meeting adjourned at 9.30.

BOSTON, May 21, 1908.

The 651st regular meeting and the 46th ANNUAL MEETING of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, May 21, at eight o'clock, about one hundred and ten persons being present. Dr. A. A. Noyes presided.

The minutes of the last meeting were read by the Secretary and approved.

The report of the Executive Committee was presented by the Secretary for the Executive Committee.

Report of the Executive Committee of the Society of Arts

The report of the Executive Committee of the Society of Arts of a year ago entered somewhat at length into the purposes of the Society and its relation to the Institute and the public.

That the Society has not for a series of years fulfilled its purposed function has been only too manifest, and this condition of affairs has been an anxiety to those charged with the conduct of its affairs.

The absence of a permanent President would seem to have contributed to the delay in formulating an active and persistent policy, but it is hoped during the coming year some systematic effort may be made to enable the Society to take its proper place in this community.

It is hoped that the Committee of the Corporation on the Society of Arts may join with your Executive Committee to this end.

During the year twenty-one (21) members have been dropped for nonpayment of dues, nine (9) have resigned, chiefly as the result of persistent efforts to collect dues in arrears, one (1) has died, and two (2) have been elected to membership. There are at present two hundred and ninety-four (294) associate members, forty-six (46) of whom have paid twenty (20) or more annual assessments and are entitled to the benefits of life membership without further payment of dues.

The attendance at the meetings has been fairly good. Eighteen (18) has been the smallest, and two hundred and twenty (220) the largest audience, with fifty (50) or sixty (60) a fair average.

There have been thirteen (13) meetings this winter, with talks on the following topics:

"Chilled Car Wheels," by Mr. F. A. Beebee, Assistant Manager of the Griffin Wheel Company, Chicago.

"Physical History of the Grand Cañon District," by Professor D. W. Johnson, of Harvard University.

"Refrigeration," by Mr. Norman H. Cheney, Chief Engineer of the Merchants' Cold Storage and Freezing Company, Providence, Rhode Island.

"Forestry," by Mr. Philip W. Ayers, State Forester of New Hampshire.

"Denatured, or Industrial, Alcohol," by Rufus F. Herrick, Chemist, of Boston.

"Ascents of Orizaba and Colima, Two Mexican Volcanoes," by Professor John E. Wolff, of Harvard University.

"The Evolution of Bogoslof, a New Volcano in Behring Sea," by Professor Thomas A. Jaggar, Jr., Institute of Technology.

"The Curtis Steam Turbine," by Mr. Charles B. Burleigh, of the General Electric Company, Boston.

"Recent Developments in Fire Protection Devices," by Mr. Gorham Dana, of Boston.

"The Lumière Autochrome Plates," by Mr. J. E. Brulatour, of the Lumière Company, New York.

"The Deflocculation of Nonmetallic Amorphous Bodies, with Special Reference to Graphite as a Lubricant," by Mr. E. G. Acheson, President of the Acheson International Graphite Company of Niagara Falls.

"Factors Governing the Rates of Public Service Corporations and the Government Control of Rates," by Professor D. C. Jackson, Institute of Technology.

"The Quebec Bridge Disaster," by Professor George F. Swain, Institute of Technology.

Your Committee earnestly desires any suggestions as to methods by which the work of the Society may be made of benefit to the community and to the Institute of Technology.

The report was accepted.

Mr. I. K. Litchfield was duly elected to associate membership.

W. S. Leland was elected Secretary, and the following members of the Executive Committee for the year 1908–09: Colonel Edmund H. Hewins, Mr. W. S. Johnson, Mr. I. K. Litchfield, Professor W. H. Walker, Dr. C. J. H. Woodbury.

There being no further business to be presented at the meeting, the chairman introduced Professor George F. Swain, Head of the Civil Engineering Department, Institute of Technology, who spoke on "The Quebec Bridge Disaster." Professor Swain explained the different forms of bridge construction, and showed the fundamental principles which are required in a safe design. He showed a large number of slides of substantial and typical bridges, and then showed slides showing the detail and general construction of the Quebec Bridge. He clearly explained the reason of collapse, and how the lattice work which failed

in this bridge compared in relative size and strength to the lattice work on other bridges which have proved satisfactory for a number of years. The lecture was most interesting and instructive, and the chairman extended the thanks of the Society to the speaker. The meeting adjourned at 9.30.

WALTER S. LELAND, *Secretary.*

BOOK REVIEWS

Standard Handbook for Electrical Engineers[1]

It is impossible within the limits of a review to give any detailed comment on the contents of a comprehensive handbook such as the new "Standard Handbook for Electrical Engineers." The value of the material is largely affected by its availability, and in this case the general arrangement is good and the index seems to be very complete. The inclusion of certain general tables omitted from some similar handbooks is a distinct advantage. The diagrams are the least satisfactory feature of the book, as many of them are too much reduced in size or too crowded to be quickly intelligible, and others are lacking in the sharpness which might reasonably be expected. The rapidity with which the first edition of this book is being exhausted is a conclusive proof that it meets a widespread demand. C. H. P.

Mining and Metallurgy in South Africa[2]

The bound volume of the Proceedings of the Chemical, Metallurgical, and Mining Society of South Africa is always a welcome addition to the literature of mining and metallurgy. Volume IV, covering the period of July, 1903, to June, 1904, was published in Johannesburg early this year.

Among the papers which are printed, with complete discussion on each, we find two or three papers on Hygiene of Mining, including the Relation of Mine Gases to Tuberculosis, Ventilation of Deep Levels, and Ankylostomiasis, and another which may perhaps be classed with these, on the Composition of Tobacco Smoke.

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[1] Standard Handbook for Electrical Engineers. New York: McGraw, 1908. 20 + 1,283 pp., il., 16mo. $4.00.

[2] Chemical, Metallurgical, and Mining Society of South Africa. Proceedings, Vol. IV, 1903-04, with Appendix. Johannesburg, Transvaal. Published by the Society, 1908.

There are two papers on Rock Crushing, considered with reference to the wet and the dry process, respectively; and a paper on Slime Treatment. The Cyanide Process naturally receives a large portion of the attention of the Society, the present volume containing no less than eight papers on various aspects of this process.

The Manufacture of Explosives, Hauling and Transportation of Ore, Smelting and Cupellation, and the Flow of Water also receive attention in this volume.

The appendices contain Minutes of the Proceedings of the Society, Report of the Committee on Cyanide Poisoning, Contributions and Correspondence, Obituary Notices, and Notices and Abstracts of Articles and Papers, classed under Chemistry, Metallurgy, Mining, and Miscellaneous.

The volume closes with Index of Authors and Subjects.

PUBLICATIONS[1]

Architecture

Truman H. Bartlett.—Essay on the Portraits of Lincoln, in Carl Schurz's Biographical Essay on Abraham Lincoln. Boston: Houghton, Mifflin & Co. December, 1907. pp. 134. 18 il. 4to.

Contains Carl Schurz's brief biography of Lincoln; essay on the portraits of Lincoln by T. H. Bartlett, illustrated by 18 photogravure prints of portraits, life mask, and hands of Lincoln; sonnet on the mask of Lincoln by R. W. Gilder; poem on the hand of Lincoln by E. L. Stedman.

The book follows, in general form, the recent editions of the Life of Cardinal Woolsey and the Autobiography of Benjamin Franklin, published by Houghton, Mifflin & Co.

Biology

S. C. Prescott and *C.-E. A. Winslow.*—Elements of Water Bacteriology, with Special Reference to Sanitary Water Analysis. Edition 2. New York: John Wiley & Sons. 1908.* pp. 12 + 258. 1 il. 12mo.

S. C. Prescott and *C.-E. A. Winslow.*—The Relative Value of Dextrose Broth, Phenol Broth, and Lactose Bile as Enrichment-Media for the Isolation of Bacillus coli. *American Journal of Public Hygiene,* Vol. 18, pp. 19–26. February, 1908.

Burt R. Rickards.—(1) Sputum Shaking and Sedimenting Apparatus. (2) A Rabies Collecting Outfit. *Journal of Infectious Diseases,* pp. 119–122. il. May, 1907.*

Burt R. Rickards.—Diphtheria, Sewer Gas, and Infection. Editorial in *American Journal of Public Hygiene,* Vol. 17, pp. 262–267. August, 1907.*

Burt R. Rickards and *H. W. Hill.*—Milk Commissions of the United

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[1] In order that the extent of productive work carried on at the Institute may be better known, it is proposed to publish quarterly a list of the publications of officers of the Institute, together with abstracts when possible. In this list the publications are arranged alphabetically by departments and then alphabetically by authors.

The asterisk after the title indicates that a copy of the publication has been placed in the library of the Institute.

States—A Synopsis of Their Work. Editorial in *American Journal of Public Hygiene,* Vol. 17. May, 1907.*

Chemistry and Chemical Engineering

F. J. Moore and *R. D. Gale.*—The Colored Salts of Schiff's Bases—(1) The Hydrochlorides of Bases Formed by Condensing p-Amino Dimethylaniline with Aromatic Aldehydes. *Journal of the American Chemical Society,* pp. 394–403, Vol. 30. March, 1908.* (Reprinted, *ante,* p. 200.)

Ellwood B. Spear.—Catalytic Decomposition of Hydrogen Peroxide under High Pressures of Oxygen. *Journal of American Chemical Society,* pp. 195–208. il. Vol. 30. February, 1908.

The article is a condensed translation of a dissertation, Heidelberg, 1907.

The chief results are:

A method has been worked out and an apparatus designed whereby rates of reaction may be measured under high gas pressures.

It has been experimentally determined that the catalytic decomposition of hydrogen peroxide by colloidal solutions of platinum, palladium, iridium, gold, and silver is inappreciably affected by increasing the pressure of the oxygen gas above the reaction-mixture from 1 to 200 atmospheres.

A. A. Noyes, W. C. Bray, and *E. B. Spear.*—Contributions from the Research Laboratory of Physical Chemistry, No. 23: A System of Qualitative Analysis for the Common Elements. Part III. Analysis of the Aluminum and Iron Groups. *Technology Quarterly,* Vol. 21, No. 1. pp. 14–125. March, 1908.*

Edward W. Washburn.—The Theory and Practice of the Iodometric Determination of Arsenious Acid. *Journal American Chemical Society,* Vol. 39, pp. 31–45. il. January, 1908.*

From a consideration of the equilibria involved in a solution containing iodine and arsenious acid, it is shown that in order that the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^-$$

shall proceed quantitatively toward the right, it is necessary that the concentration of hydrogen-ion in the solution at the completion of the titration shall be close to 10^{-7} molal. It is shown that mixtures of sodium bicarbonate and carbonic acid, borax and boric acid, or disodium phosphate and phosphoric acid in the proper proportions will automatically maintain the concentration of hydrogen-ion at the desired value. Identical results are obtained with each of these mixtures, but the phosphate mixture is to be preferred, owing to the non-volatility of the

acid. When the proper conditions are fulfilled, it is shown that the titration of arsenious acid with standard iodine solution can be made with an accuracy of 0.002 per cent., and that the end point is exceedingly delicate and absolutely permanent. Directions are given for preparing the standard solutions and carrying out the titration in order to attain the above mentioned accuracy.

Civil Engineering

C. B. Breed.—Abolition of Grade Crossings at Worcester, Mass. *Railroad Gazette,* Vol. 14, No. 11, pp. 358–461. il. March 13, 1908.

G. A. Goodenough and *L. E. Moore.*—The Strength of Chain Links. *University of Illinois Publications, Bulletin Engineering Experiment Station.* Vol. 5, No. 1, pp. 73. il. September 2, 1907.

George E. Russell.—Notes on Hydraulics. Boston, December, 1907. pp. 80. il.

Drawing

C. W. Sawyer.—Vacation on a Way-Back Farm. *Forest and Stream.* February 25, 1899.

C. W. Sawyer.—Three Rifles and a Shotgun. *Forest and Stream.* August 10, 1901. il.

C. W. Sawyer.—Experimenting with a Ballard. *Shooting and Fishing.* January 1, 1901.

C. W. Sawyer.—Twenty-two Calibre Experimenting and Notes. *Shooting and Fishing.* October 17 and 24, 1901.

C. W. Sawyer.—The Mystery of a Bullet. *Recreation.* July, 1902.

C. W. Sawyer.—Experimenting with a Ballard with Kent Treatment. *Shooting and Fishing.* January 1, 1903. il.

Electrical Engineering

Dugald C. Jackson and *William B. Jackson.*—Inventory and Valuation of the Property of the Minneapolis General Electric Co., Minneapolis, Minn. Chicago, December 4, 1907.*

Dugald C. Jackson.—Report to the Massachusetts Highway Commission, being an answer to three questions asked by the Commission growing out of the investigation of the New England Telephone & Telegraph Co. Boston, March 10, 1908. pp. 26.*

W. V. Lyon.—Notes on the Parallel Operation of Alternators. *Electrical World,* Vol. 50, pp. 1243–1246. il. December 28, 1907.

Notes on the Parallel Operation of Alternators, by Mr. W. V. Lyon, is a purely theoretical treatment of this subject. The results which he arrives at will, of course, differ more or less from actual practice; depending upon the condition of actual operation, the characteristics of the machines, etc.

The author finally obtains an equation for the synchronizing current. This enables him to deduce a number of interesting conditions which effect the operation of alternators in parallel.

Charles H. Porter.—What Will Congress Do? *Technology Review,* Vol. 10, No. 1, 1908.*

Charles H. Porter.—Standard Polyphase Apparatus and Systems. Book Review in *Technology Quarterly,* Vol. 20, No. 4, 1907.*

Harrison W. Smith.—Demonstration Apparatus for Illustrating Commutation. *The Electrician,* Vol. 60, pp. 509–510. il. January 17, 1908.* (Reprinted, *ante,* p. 178.)

C. J. H. Woodbury.—Electric Light and Power in Telephone Service. *Electrical Record,* pp. 132–134. il. March, 1908.

C. J. H. Woodbury.—The Purpose of Commercial Organization. An address before the American Association of Woolen and Worsted Manufacturers. Philadelphia, Pa., December 6, 1907. pp. 11.*

English

Arlo Bates.—The Intoxicated Ghost and Other Stories. Boston: Houghton, Mifflin & Co. April 25, 1908. 3 + 303 pp. 8vo.

Allen French.—The Weaker Vessel. *Appleton's Magazine.* January, 1907.

Allen French.—Salad Plants. *Suburban Life.* March, 1908.

Allen French.—A Garden Lesson. *Woman's Home Companion.* April, 1908.

Geology

H. W. Shimer and *Mildred E. Blodgett.*—The Stratigraphy of the Mt. Taylor Region, New Mexico. *American Journal of Science,* pp. 53–67, Vol. 25. January, 1908.

Describes the strata lying immediately east of Mt. Taylor, New Mexico, giving lists of fossils from different localities. The fossils, including two new varieties, are discussed specifically. It is noted that these faunæ contain prominent dwarfed species, and are thus suggestive of unfavorable seas in the area during this portion of the upper Cretaceous.

History and Economics

D. R. Dewey.—Review of "The Tariff and the Trusts," by Franklin Pierce. *American Historical Review.* July, 1907.

D. R. Dewey.—Review of "John Sherman," by T. E. Burton. *American Historical Review.* July, 1907.

D. R. Dewey.—Financial History of the United States. Edition 3. Longmans, Green & Co. November, 1907.

Mathematics

N. J. Lennes and *H. E. Slaught.*—High School Algebra, Advanced Course. Boston, April 1. pp. 200.

Mechanical Arts

William G. Snow.—Principles of Heating. New York: David Williams Co. 1907. pp. 161.

Modern Language

John Bigelow, Jr.—Review of "Leading American Soldiers," by R. M. Johnston. *American Historical Review,* pp. 366–367. January, 1908.

John Bigelow, Jr.—Review of "The Campaign of Santiago," by Capt. H. H. Sargent. *American Historical Review,* pp. 373–375. January, 1908.

Physics

H. M. Goodwin and *R. D. Mailey.*—On the Density, Electrical Conductivity, and Viscosity of Fused Salts and Their Mixtures. *Physical Review,* Vol. 25, No. 6, pp. 460–489, December, 1907; and Vol. 26, No. 1, pp. 1–60, January, 1908.*

The results of our investigation may be summarized as follows:

1. The density of fused sodium, potassium, lithium and silver nitrate, and silver chlorate, together with mixtures of sodium and potassium nitrate and of lithium nitrate and silver chlorate, had been determined to 0.1 per cent. over a wide range of temperature. In all cases the density was found to be a linear function of the temperature to within a tenth of 1 per cent. Tables giving the specific and molecular volume of the above salts for every ten degrees have been computed.

2. The specific volume of mixtures of sodium and potassium nitrate containing 8 and 2, 5 and 5, and 2 and 8 mols of these salts, respectively, is greater than that computed from the specific volumes of the components, *i. e.*, the solution of one salt in another is accompanied by an expansion. The magnitude of this expansion is small, being a maximum (0.5 per cent.) for equimolecular mixtures.

In the case of an equimolecular mixture of lithium nitrate and silver chlorate, on the other hand, a contraction of 20 per cent. occurs.

3. The specific conductance of the same salts and salt mixtures has been determined over the same temperature interval as the density. The results show that, except in the case of lithium nitrate and silver chlorate, which could be measured over only a limited range of temperature on account of their instability, the specific conductance is not strictly proportional to the temperature, but increases less and less rapidly as the temperature rises. For the limited range of temperature over which lithium nitrate, silver chlorate, and their mixtures were studied the specific conductance is proportional to the temperature. Tables have been computed giving the specific and equivalent conductance of each salt and mixture for every ten degrees, as well as the temperature coefficient for each interval. The temperature coefficient is, generally speaking, less than one-fifth as great as that for the corresponding aqueous solutions.

4. A study of the computed values of the equivalent conductance shows that this quantity increases very nearly linearly with the temperature. The temperature coefficient decreases, therefore, with increasing temperature, but at any given temperature is slightly greater than that of the specific conductance at the same temperature.

5. The equivalent conductance of the mixtures of the sodium and potassium nitrate is less than that computed from the equivalent conductance of the components. This is most marked in the case of the equimolecular mixture where the difference reaches 3 per cent., an amount considerably greater than can be accounted for by experimental error. It tends to confirm the view that the effect of dissolving one nitrate in another is to decrease the dissociation. Our results do not confirm the conclusion drawn by Poincaré from similar experiments on the conductivity of mixed nitrates, namely, that the conductance of a mixture can be accurately calculated from that of the components by the mixture formula.

6. In the case of an equimolecular mixture of lithium nitrate and silver chlorate, the deviations between observed and computed values of the equivalent conductance are as much as 12 per cent., the computed values being, as before, the larger, indicating a metathesis between the components with corresponding change (decrease) of ionization. This mixture also showed a contraction in volume of 16 per cent.

7. The fluidity, or reciprocal of the absolute viscosity coefficient, of the same series of fused salts was measured over the temperature interval in which their conductivity and density were studied.

In all cases the fluidity was found to be directly proportional to the temperature. Its temperature coefficient is in every case greater than the corresponding temperature coefficient of specific conductance.

8. The ratio

$$\frac{\text{specific conductance}}{\text{fluidity}} = \frac{\kappa}{F},$$

computed for every ten degrees was found to decrease regularly, without exception, with increasing temperature. Foussereau's law of the proportionality between these quantities is, therefore, not confirmed. Our results are, however, in excellent agreement, so far as comparison is possible, with those of Lorenz and Kalmus.

9. The value of

$$f = \frac{\text{fluidity}}{\text{molecular volume}} = \frac{F}{\phi},$$

which we have called molal fluidity, and its temperature coefficient for each ten degrees were also computed. The results show that the molal fluidity is directly proportional to the temperature. The ratio

$$\frac{\text{molal conductance}}{\text{molal fluidity}} = \frac{\Lambda}{f}$$

has also been calculated for every ten degrees. This ratio is practically a constant for potassium nitrate and mixtures of potassium and sodium nitrate over a range of temperature of more than 100 degrees. In the case of sodium, lithium, and silver nitrates the proportionality does not hold quite as rigidly; the ratio decreases with increasing temperature by a small percentage, an amount, however, which we believe cannot be attributed wholly to experimental error. The ratio is approximately a constant for the group of nitrates investigated.

From this it appears, if proportionality between mobility of ions and fluidity be assumed, that increasing the temperature of the fused salts investigated has little effect on their ionization; its tendency is to decrease rather than increase their electrolytic dissociation—a result analogous to the effect on salts in aqueous solutions raised to high temperatures under pressure, as recently shown by Noyes. As this is characteristic of very highly dissociated substances, our results lend weight to the view that a high rather than a low degree of ionization obtains in fused electrolytes.

10. The molal fluidity of mixtures of sodium and potassium nitrate is greater than that computed from the components of the mixture. The difference is nearly constant for a given mixture, *i. e.*, independent of the temperature; it is greatest for equimolecular mixtures. As the equivalent conductance of these same mixtures was found to be less than the calculated values, we have additional evidence that the effect of increased fluidity on the migration velocity of the ions is probably more than neutralized by a diminished dissociation of the mixed salts.

11. The results of this investigation provide a more fundamental experimental basis for the further development of the theory of conduction in fused salts than has hitherto been possible. Although the accumulation of these data is laborious, as it involves three independent investigations on density, conductivity, and viscosity, all of which are of more than ordinary difficulty if a precision better than

1 per cent. is desired, it is to be hoped that other contributions to this important and interesting field of electro-chemistry will be made in the near future.

M. de Kay Thompson and *M. W. Sage.*—On the Free Energy of Nickel Chloride. *Journal American Chemical Society,* pp. 714–720, Vol. 30. May, 1908.* (Reprinted, *ante,* p. 190.)

Institute Publications

Massachusetts Institute of Technology.—President's Report. Bulletin of the Massachusetts Institute of Technology, Vol. 43, No. 2. pp. 161. Boston, January, 1908.*

Massachusetts Institute of Technology.—Advanced Study and Research. Bulletin of the Massachusetts Institute of Technology, Vol. 43, No. 1, Pt. 2. pp. 41. Boston, February, 1908.

Massachusetts Institute of Technology.—Summer Courses. Bulletin of the Massachusetts Institute of Technology, Vol. 43, No. 2, extra number. pp. 15. Boston, March, 1908.

Massachusetts Institute of Technology.—Register of Graduates. Bulletin of the Massachusetts Institute of Technology, Vol. 43, No. 3. pp. 401. Boston, March, 1908.*